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THE INCREASE IN THE RADIATION INTENSITY OF METALS IN A FLAME AS A RESULT OF IONIZATION SUPPRESSION

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It is well known that when the vapors of two or more alkali metals which have low ionization potentials (K, Rb, Cs) are introduced into a flame, the radiation intensity of each of them increases to a value which is greater than when only one metal is present [1-2]. This phenomenon which is used for increasing the sensitivity of Cs determination [3-5] is explained by ionization suppression [6-11]. When the flame temperature is high enough, metal atoms which are formed as a result of thermal dissociation of the salts introduced are partially ionized in accordance with the equation $Me \rightleftarrows Me^+ + e^-$ (e^- is an electron). As a result, the partial pressure of the neutral atoms of the metal, which are responsible for the radiation of the resonance lines of the metal, is lower than the value to be expected in the absence of ionization. Addition of other ionizing metals which increase the partial pressure of the electrons in in the flame displaces the ionization equilbrium, while the partial pressure of the neutral atoms, and consequently the radiation intensity of their resonance lines connected with this, increases. At the same time there is a possibility of an interaction between the atoms of the test metal and atoms or radicals arising from the acid residue of the salt in the form of which the other metal is added, and a decrease, as a consequence of this, in the partial pressure of the atoms of the first metal (development of the anion effect). Nevertheless, in some cases (nitrates and hydroxides) this effect is negligibly small, and the resulting change in radiation intensity can be ascribed simply to the shift in ionization equilibrium. Hitherto no attempts have been made to develop theories which express the mutual effect of one ionizing metal on the radiation intensity of another in quantitative terms, using the hypothesis of the ionization of atoms as a basis.

Theory. First of all let us consider the ionization of one metal in a flame. The degree of ionization α_0, i.e., the ratio of the partial pressure of the ions P_{Me^+} to the total partial pressure P_N of the ions and nonionized metal ions P_{Me} introduced into the flame ($P_M = P_{Me} + P_{Me^+}$) can be calculated as follows. According to the ionization equation

$$\frac{P_{Me^+} \cdot P_{e^-}}{P_{Me}} = K_{ion}, \qquad (1)$$

where P_{e^-} is the partial pressure of the electrons, K_{ion} is the ionization constant of the metal determined from the relationship:

$$\lg K_{ion} = -\frac{23053I}{4{,}573T} + \frac{5}{2}\lg T - 6{,}49 + \lg\frac{g_{Me^+} \cdot g_{e^-}}{g_{Me}},$$

where I is the ionization potential of the atoms, ev; T is the flame temperature; g_{Me^+}, g_{e^-}, g_{Me} are the statistical weights of the ions, electrons, and neutral atoms. In the case of one metal $P_{e^-} = P_{Me^+}$. Substituting in equation (1) this value P_{e^-} and the values $P_{Me} = P_N - P_{Me^+}$, we get

$$\frac{(P_{Me^+})^2}{P_N - P_{Me^+}} = K_{ion}, \qquad (2)$$

from which

$$\alpha_0 = \frac{P_{Me^+}}{P_N} = \frac{\sqrt{4a+1}-1}{2a}, \qquad (3)$$

where

$$a = P_N/K_{ion}.$$

Thus the degree of ionization α_0 for various atoms depends only on the ratio of the total partial pressure of the metal atoms introduced into the flame to the ionization constant. Fig. 1 shows the relation between the value of $P_{Me}+/P_N$ (in %) and the logarithm of the ratio P_N/K_{ion}. It is clear from the figure that the degree of ionization α_0 approaches zero for $P_N/K_{ion} > 1000$ [$\lg(P_N/K_{ion}) > 3$] and approximates to 100% for $P_N/K_{ion} < 0.01$ [$\lg(P_N/K_{ion}) < -2$].

It was interesting to establish the values of the degree of ionization for various real conditions by flame photometry. The total partial pressure of the metal atoms and ions in the gas flame depends on the concentration of metal salt in solution (C,M), the efficiency of the sprayer, the type of gas, amount of gas supplied to the burner in unit time, the temperature of the flame, and also on the extent to which the atoms and ions are combined as gaseous hydroxide molecules. Under the conditions used in the present work [12], the following relationships hold for the total partial pressure of the metal atoms which would be in the flame if there was no ionization, and if no molecules of gaseous hydroxides were formed:

$$P_{N'} = C \cdot 10^{-3.7} a T \text{ (acetylene flame)} \quad (4)$$

$$P_{N'} = C \cdot 10^{-4.78} a T \text{ (illuminating gas flame)} \quad (5)$$

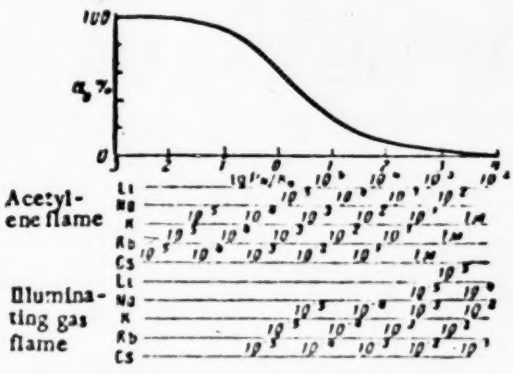

Fig. 1. Degree of ionization α_0 (in %) as a function of the log of the ratio P_N/K_{ion}. The values of the concentration of alkali metals in solution (M) are given under the curve for an acetylene flame and for illuminating gas flame; these values correspond to definite values of P_N/K_{ion} in the flame.

These relationships were derived on the assumption that the concentration of metal atoms in the flame [13] [N_{total}] = $6.2 \cdot 10^{14} \cdot C$ atoms/ cm^3. The equilibrium of the formation of hydroxide molecules conforms to the equation

$$\frac{P_{Me} \cdot P_{OH}}{P_{MeOH}} = K_{dissoc.}$$

where P_{OH} and P_{MeOH} are the partial pressures of hydroxyl radicals and metal hydroxide, and $K_{dissoc.}$ is the dissociation content of the latter. At not very high salt concentrations, the value of P_{OH} is several times smaller than P_{Me} and P_{MeOH}, and can accordingly be assumed to be constant. From this:

$$\frac{P_{Me}}{P_{MeOH}} = \frac{K_{dissoc.}}{P_{OH}} \text{ const} \quad (6)$$

while the following relation is also constant

$$\frac{P_{Me}}{P_{MeOH} + P_{Me}} = \frac{P_{Me}}{P_{N_{total}}} = \beta \quad (7)$$

β, which is the extent of dissociation of alkali metal hydroxides, has been studied very little. For the flame of an acetylene – air mixture $\beta = 1$ in the case of sodium, since it does not form a stable hydroxide. In the case of the remaining metals, the tendency to form stable hydroxides increases in the order K, Rb, Cs, Li. The value of β for K = 0.43 while for Li β = 0.21. It should be noted that the value of β does not differ strongly from 1 and can be left out in further discussion. As for the concentration of metal in solution, we used the relationships (4) and (5) and the values of K_{ion} from Sakh's formula (Table 1).

These results are given in Fig. 1. As the figure shows, for the case of lithium and sodium in an illuminating gas flame, the fraction of ionized atoms is small, and neutral atoms are present in the main. In the case of potassium, ionization should become observable even at low concentrations $10^{-4} - 10^{-5}$ M, while it should be appreciable for rubidium and cesium over the same concentration range. In an acetylene flame ionization should be high for K, Rb, and Cs over the concentration range normally used in analysis, and should be observable even for lithium over the concentration range $10^{-4} - 10^{-5}$ M. Nevertheless, in actual fact, a limit is set on the ionization of the metals at low concentrations by the presence in the flame gas of charged particles whose partial pressure for an acetylene–air mixture, according to [14], is about 3.6×10^{9} equal to approximately $10^{-7.45}$ atm, and according to our results about $10^{-8.5}$ atm. Since, according to expressions 4 and 5, a partial pressure of atoms P_N which is close to this value is created at $C = 10^{-4} - 10^{-5}$ M, it follows that the background of charged particles in the flame will prevent ionization of metal introduced into the flame when the metal concentration in solution is below $10^{-4} - 10^{-5}$ M, such concen-

trations not being normally used in analysis. These results relate to that part of the flame which is 10-20 mm above the inner cone; near the zone of primary combustion of hydrocarbon flames the background of charged particle is significantly higher [11] and may lead to complete supression of ionization of the alkali metal introduced into the flame [15].

TABLE 1. Values of the Logarithm of the Ionization Constant of the Alkali Metals in an Acetylene and in Illuminating Gas Flame

Metal	Logarithm of ionization constant		log P_N/K_{ion} for 1 M salt solutions	
	Illuminating gas flame, T= 1970° K	Acetylene flame, T= 2360° K	Illuminating gas flame	Acetylene flame
Lithium	−12.03	−9.52	8.25	5.32
Sodium	−11.38	−9.00	7.60	3.20
Potassium	− 9.33	−7.31	5.55	3.51
Rubidium	− 8.93	−6.96	5.15	3.16
Cesium	− 8.20	−6.35	4.42	2.55

Let us consider how the concentration of nonionized metal atoms in the flame, and the radiation intensity related to it, will increase in the presence of another metal which is capable of ionizing. In order to develop the theory further it will be expedient to introduce the concept of the maximum possible increase in radiation intensity A (in the absence of self-absorption) which occurs as a result of complete conversion of all the metal ions into neutral atoms. Thus,

$$A = P_N / P_{Me}$$

since

$$P_{Me}/P_N = 1 - P_{Me^+}/P_N, \tag{8}$$

then using the value of P_{Me^+}/P_N from (3) we find that:

$$\frac{P_N}{P_{Me}} = \frac{1}{1 - P_{Me^+}/P_N} = \frac{2\alpha}{2\alpha + 1 - \sqrt{4\alpha + 1}} = A. \tag{9}$$

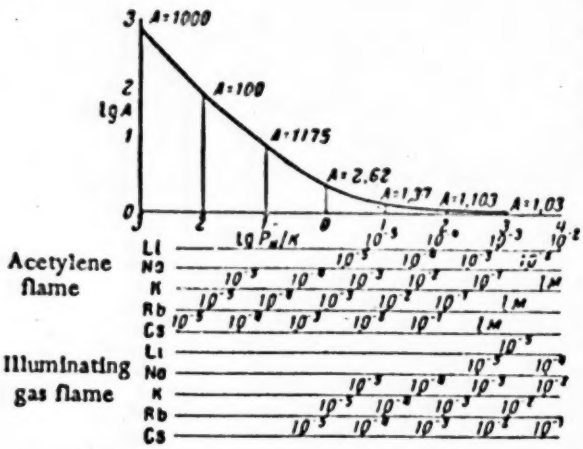

Fig. 2. The relations between the logarithm of the maximum possible increase A, following from ionization suppression, and the logarithm of the ratio P_N/K_{ion}. The concentrations of the alkali metals in solution (M) corresponding to definite values of P_N/K_{ion} in the flame are given under the curve.

The relation between log A and gP_N/K_{ion} calculated by means of this equation is shown in Fig. 2. The maximum possible increase in radiation intensity at $\alpha = 1000$ amounts in all to 0.03 (3%), while for $\alpha = 100$ it is 0.103 (10.3%), i.e., it is low. At $\alpha = 10$ it already amounts to 0.37, while at $\alpha = 1$ it is 2.62 (262%); further, it increases almost inversely proportionally to α, and amounts to 1000 at $\alpha = 0.001$.

Comparison with the scale for P_N/K_{ion} values as a function of the concentration C in solution, however, shows that in the case of an acetylene flame an appreciable increase can only be expected for three elements K, Rb, and Cs; in the case of Na and Li it is only possible (and then only to a small extent – an increase of 10-20%) at very low concentrations of the elements in solution – 10^{-4}M and lower. In an illuminating gas flame an increase may be manifested to a small extent in the case of K, Rb, and Cs at very low concentrations, while there will be no increase at all in the case of Li and Na. In this connection one should bear in mind what was said above about the effect of the ionization of the flame itself.

When two metals Me_1 and Me_2 are present in the flame, the degree of ionization of each metal in the flame will be determined by three equations:

$$\frac{P_{Me_1^+} \cdot P_{e^-}}{P_{Me_1}} = K_{1ion}, \tag{10a}$$

$$\frac{P_{Me_2^+} \cdot P_{e^-}}{P_{Me_2}} = K_{2ion}, \tag{10b}$$

$$P_{Me_1^+} + P_{Me_2^+} = P_{e^-} \tag{10c}$$

In these equations P_{Me_1}, P_{Me_2}, $P_{Me_1^+}$, $P_{Me_2^+}$, P_{e^-} are the partial pressures of metal atoms, ions, and electrons, while K_{1ion} and K_{2ion} are the corresponding ionization constants. Using equations (10 a, b, c) it is possible to calculate the degree of ionization of each of the metals $\alpha = P_{Me^+}/P_N$ in the presence of the other in the flame, and from this, the relative increase as a fraction of the maximum, meaning by the latter the ratio of the increase in partial pressure of the atoms $(\alpha_0 - \alpha) \cdot P_N$ to the maximum possible $(\alpha_0 \cdot P_N)$.

In order to calculate the relative increase we substitute the value for P_{e^-} from the equation (10c) in equations (10a) and (10b):

$$\frac{P_{Me_1^+} \cdot (P_{Me_2^+} + P_{Me_1^+})}{P_{Me_1}} = K_{1ion}, \tag{11a}$$

$$\frac{P_{Me_2^+} \cdot (P_{Me_1^+} + P_{Me_2^+})}{P_{Me_2}} = K_{2ion}. \tag{11b}$$

Having assigned definite value to $P_{Me_1^+}$ for definite values of $P_{N_1}/K_{1ion} = \alpha$, we calculate $P_{Me_2^+}$; for this purpose we substitute $P_{Me_1} = P_{N_1} - P_{Me_1^+}$ in equation (11a).

$$P_{Me_2^+} = \frac{\alpha \cdot K_{1ion}^2}{P_{Me_1^+}} - K_{1ion} - P_{Me_1^+}.$$

Knowing $P_{Me_1^+}$ and $P_{Me_2^+}$, it is possible to determine P_{Me_2} from equation (11b):

$$P_{Me_2} = \frac{P_{Me_2^+} \cdot (P_{Me_1^+} + P_{Me_2^+})}{K_{2ion}}.$$

It is then possible to calculate $P_{N_2} = P_{Me_2} + P_{Me_2^+}$ and the ratio P_{N_2}/P_{N_1}. When the various values ranging from 0 to $P_{N_1} \cdot \alpha_0$ (where α_0 is the degree of ionization for one element) are given to $P_{Me_1^+}$, it is possible to obtain a series of values for P_{N_2}/P_{N_1}, corresponding to different degrees of ionization α of the main element.

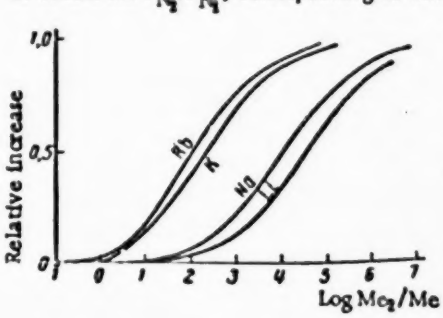

Fig. 3. The relation between the relative increase $(\alpha_0 - \alpha_1)/\alpha_0$ of cesium and the logarithm of the ratio of the concentration of the alkali metals added to cesium concentration. The cesium concentration in solution = 10^{-4} M; the maximum possible increase A = 22,3.

In order to calculate the increase which occurs on suppression of ionization, we calculate for each case the degree of ionization $\alpha_1 = P_{Me_1^+}/P_{N_1}$, and from this the relative increase $(\alpha_0 - \alpha_1)/\alpha_0$. The relative increase was calculated for cesium in this way for several cesium concentrations and one potassium concentration.

In Fig. 3 is shown one of a typical series of curves for cesium at a concentration of 10^{-4} M, using an acetylene flame (the theoretical maximum increase A=22,3). The curves for the relative increase have an S shape, while the upper and lower parts asymptotically approach the line of maximum increase and the abscissa. Curves for various metals are approximately parallel and are shifted in the middle along the abscissa by a value which corresponds approximately to the difference in

the logarithms of the ionization constants of the corresponding metals. In other words, in order to evoke an equal relative increase, the concentrations of the metals added should be inversely proportional to their ionization constants. An appreciable relative increase (> 5%) for each of the added metals is observed starting at a certain concentration below which this metal has almost no effect on radiation intensity. Thus potassium starts to show an effect from concentrations which are twice that of cesium [$\log(P_{Me_2}/P_{Me_1})$] = 0.3, while sodium starts to show an effect at concentrations about 60 times that of cesium ($\log P_{Na}/P_{Cs} = 1.8$).

In Fig. 4 are shown curves for the relative increase in cesium under the influence of potassium and sodium for three cesium concentrations in solution (10^{-3}, 10^{-4}, and 10^{-5}M); log C (M) is plotted along the abscissa, not log (P_{Me_2}/P_{Me_1}). An increase approximating to the maximum possible is not observed when the maximum concentration of the foreign metals of 1 M is used, either in the case of K or Na. Thus in the case of the latter element at $C_{Cs} = 10^{-4}$ and 10^{-5} M and $C_{Na} = 1$M, the increase is only half of the maximum possible. A conclusion of practical importance which can be drawn from this is that buffering with sodium salts does not lead to the desired results, and that the presence of additional amounts of potassium and rubidium salts in the solution will lead to an additional increase in the intensity of the cesium line. It is clear from Fig. 4 that at equal concentrations potassium or sodium affect the radiation intensity to the same extent when the cesium concentration is 10^{-4}-10^{-5} M; thus an equal increase in the relative intensity of the Cs line is obtained for different Cs concentrations. At $C_{Cs} = 10^{-3}$M, the effect of K and Na is weaker and a higher salt concentration is necessary to give the same relative increase. This fact is important for explaining the path taken by the curves relating the line intensity of the ionizing metal and its concentration in the presence of various constant concentrations of the other metal.

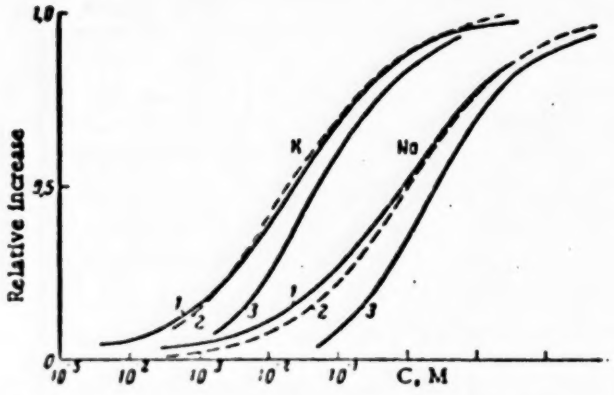

Fig. 4. The relation between the relative increase in cesium $(\alpha_0 - \alpha_1)/\alpha_0$ and the concentration of potassium and sodium salts in solution. 1) 10^{-3} M Cs; 2) 10^{-4} M Cs; 3) 10^{-5} M Cs.

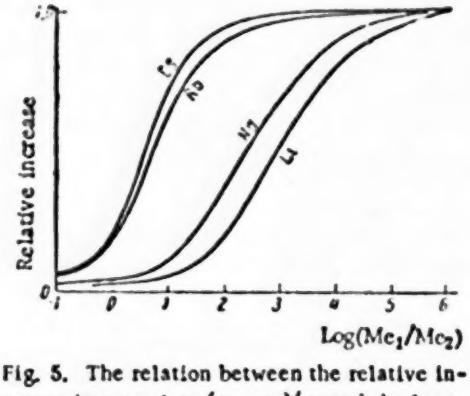

Fig. 5. The relation between the relative increase in potassium $(\alpha_0 - \alpha_1)/\alpha_0$ and the logarithm of the ratio of the concentration of the added alkali metals to potassium concentration ($C_K = 10^{-4}$M, A = 4.2).

Let us also consider the case of the effect of alkali metal salts on the radiation intensity of potassium. The potassium concentration chosen for calculation was 10^{-4}M, while the maximum increase = 4.2 for an acetylene flame. As is evident from Fig. 5, cesium at a concentration ratio Cs:K as low as 100-200 (i.e. at a cesium concentration of $1 - 2 \cdot 10^{-2}$M) leads to almost complete supression of ionization; under these conditions the relative increase amounts to 0.95. In the case of Na and Li, concentrations of 10-20 M ($\log P_{Na}/P_K = 5.05$-5.3) are necessary to achieve the same end; at ordinary salt concentrations of the order of 1 M complete supression of ionization is not obtained.

Verification of the Calculations. In order to check on the conclusions derived from theory, experiments were carried out on the effect of K, Na, and Li on the radiation intensity of cesium in an acetylene flame. A comparison was made of the readings obtained for cesium radiation at 852.1 mμ on a flame spectrophotometer composed of a UM-2 monochromator, a photomultiplier, and a microammeter [5] when solutions of cesium salts (10^{-4} and 10^{-3}M) were sprayed directly into the flame, and the readings obtained when the same solutions to which Na, K, and Li salts had been added at concentrations of 10^{-4}, 10^{-3}, 10^{-2}, 10^{-1} and 1 M were sprayed into the flame. In order to eliminate the "anion effect" solutions of the nitrates of the alkali metals were used. The radiation intensity of Cs solutions to which no foreign salts had been added was taken as 100%. The results are given in Table 2.

The results are presented graphically in Fig. 6, a logarithmic scale being adopted for the concentrations of the alkali metals added.

The curves obtained have the shape of the initial branches of the S-shaped curves in Fig. 4.

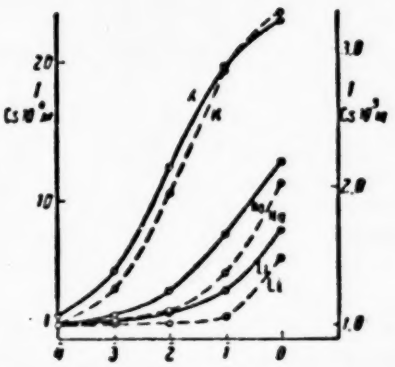

Fig. 6. The relation between the intensity of the cesium line and the logarithm of the concentration of added alkali metals. Continuous line: $C_{Cs} = 10^{-4}$M; dotted line: $C_K = 10^{-3}$M.

TABLE 2. Change in the Radiation Intensity of Cesium in an Acetylene Flame in the Presence of Other Alkali Metals

Concentration of alkali metal added, M	Relative intensity of the cesium line: at a Cs concentration of 0.0001 M in the presence of the metals			at a Cs concentration of 0.001 M in the presence of the metals		
	Li	Na	K	Li	Na	K
0,0001	103	105	150	100	100	100
0,001	119	145	444	100	105	125
0,01	170	352	1200	100	107	195
0,1	340	765	1980	105	140	290
1,0	780	1270	2350	150	205	325

In order to determine more accurately the maximum possible increase on the basis of the results given in Table 2, a curve of log relative intensity against $1/\sqrt[4]{C}$ was constructed. This relation was used because it is possible to extrapolate to C = ∞ (Fig. 7) more readily.

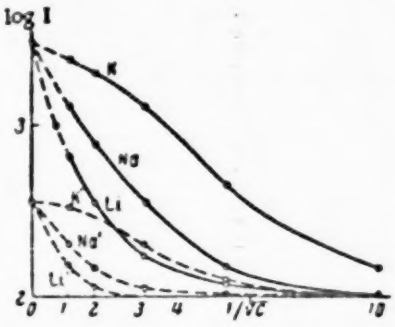

Fig. 7. The relation between the logarithm of the intensity of the cesium and $1/\sqrt[4]{C}$ (C is the concentration of added alkali metals). Continuous line: $C_{Cs} = 10^{-4}$M; dotted line: $C_{Cs} = 10^{-3}$M.

According to Fig. 7 the maximum increase at C = ∞ ($1/\sqrt[4]{C} = 0$) amounts to 28.0 for $C_{Cs} = 10^{-4}$M, and to 3.63 for $C_{Cs} = 10^{-3}$M instead of the calculated values of 22.3 and 3.64 respectively. There is therefore a reasonably close agreement between the calculated values obtained on the basis of theory and the experimental results.

In conclusion it is interesting to consider the possible increase in the radiation of the alkaline-earth metals in a flame following upon ionization supression. The logarithms of the ionization constants of the alkaline-earth metals in an acetylene flame, according to Sakh's formula [12] are: for Ca = -10.45, for Sr = -9.55, and for Ba = -8.55. The degree of dissociation of the oxide (or hydroxide) compounds must be taken into account in view of their small values; we take the values [13] Ca = $4.7 \cdot 10^{-2}$, Sr = $1.1 \cdot 10^{-1}$ and Ba = $2.1 \cdot 10^{-3}$. From this, the ratio P_N/K_{ion}, on the basis of (4) and (7) amounts to $10^{5 \cdot 6}C$ for Ca, $10^{4 \cdot 89}C$ for Sr and $10^{2 \cdot 17}C$ for Ba (C is the concentration of the metal in the form of its salt in solution, M). In the case of salt solutions with concentrations of 1 and 0.1 M (C = 1 and 0.1), for Ca and Sr we obtain, on the basis of the curves (Figs. 1 and 2) a negligible degree of ionization, and an almost unobservable maximum possible increase as a result of ionization supression; in actual fact it was not observed experimentally [16]. Under these conditions, in the case of Ba, however, the value would be appreciable.

SUMMARY

The quantitative relations which hold during the increase in the radiation intensity of a metal in a flame as the result of ionization supression due to the presence of another metal have been considered. The degree of ionization of the metal atoms in the flame and the maximum possible increase following from complete conversion of ions into nonionized atoms depend on the ratio of the total partial pressure of atoms and ions in the flame to the ionization constant. The characteristic effects shown by other alkali metals on the radiation intensity of the test metal have been established. The theoretical deductions have been confirmed, taking as an example the increase in radiation intensity of cesium caused by the presence of other alkali metals in the flame of an acetylene-air mixture.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

A FLUORESCENCE METHOD FOR DETERMINATION OF MICROAMOUNTS OF METALS IN THE FORM OF METAL-THIOCYANATE (HALIDE)–BASIC DYE COMPOUNDS

COMMUNICATION 1. DETECTION OF ZINC ON THE BASIS OF THE FLUORESCENCE EXTINCTION OF AQUEOUS SOLUTIONS OF RHODAMINE C

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Rhodamine C (rhodamine B in the old nomenclature) is a valuable reagent for the photometric, extraction-photometric, and fluorescent determination of microamounts of gallium, thallium, indium, antimony, tungsten, etc. Methods for the detection and photometric determination of zinc with rhodamine C have been described [2-4]. On interaction with metals, sparingly soluble compounds $A_2[MeHal_4]$ are formed, in which A is the cation of the basic dye, Me is the metal, and Hal is halide or thiocyanate. It has been noted [4] that formation of the zinc thiocyanate rhodamine compound leads to extinction of the fluorescence of rhodamine C.

Our problem was to study the possibility of determining zinc in the form of a thiocyanate compound with rhodamine C by a fluorescent method. Our experiments confirmed published information [4] on the extinction of rhodamine C fluorescence. As the zinc concentration increases, the color of the fluorescence changes from orange to red. It should be possible therefore to develop a method for determining zinc on the basis of measurement of the fluorescence extinction of aqueous solutions of rhodamine C.

Fluorescence intensity was measured on an FM photometer of the Pulfrich type. A PRK-4 tube fitted with a UFS-3 filter 40 × 40 mm was used as the fluorescence excitation source.

Fluorescence extinction, like the change in color which is observed during formation of the zinc thiocyanate rhodamine compound, depends on a number of factors which have not been studied sufficiently. pH and thiocyanate concentration are the most important factors.

It was found that thiocyanate ions will lead to fluorescence extinction of rhodamine C in the absence of zinc, and also cause the color to change from orange to red, as well as causing a change in the color of rhodamine C from red-violet to blue. Published results on the interaction between thiocyanate ions and rhodamine C are contradictory, [1,2]. Accordingly, we carried out experiments under such conditions which ensured absence of zinc and other heavy metals present as impurities in the reagents and in the distilled water; the latter were purified beforehand with dithizone. These experiments confirmed published results [2] to the effect that thiocyante ions give a color reaction with rhodamine C, similar in its outward effect to the reaction of zinc thiocyanate ions.

In order to establish the optimum conditions for determining zinc, we next studied the relation between the formation of the two compounds, thiocyanate-rhodamine and zinc thiocyanate rhodamine, which can be formed in the zinc thiocyanate-rhodamine C system, and the pH and thiocyanate concentration.

These experiments showed that as the result of formation of zinc thiocyanate-rhodamine and thiocyanate-rhodamine the solutions become turbid; the fluorescence is, however, stable with time and there is no need to add a stabilizer. To get reproducible results and maximum fluorescence extinction of the rhodamine C, it is necessary to mix the solutions of zinc, thiocyanate, rhodamine C and water (to a definite volume). In all subsequent measurements, we kept to this order of adding the solutions.

The relation between the fluorescence of the system zinc thiocyanate rhodamine C and pH is shown in Fig. 1. A red filter was used for measuring the fluorescence; the reference solution was a solution of $1.6 \cdot 10^{-5}$M rhodamine C in a medium of 0.17 M potassium thiocyanate; the fluorescence of this solution was taken as 100%.

As Fig. 1 shows, at pH>6 determination is in general impossible. This is connected with the state of the rhodamine (a pseudo base is formed), since under these conditions, in dilute solutions, neither the zinc thiocyanate ion nor the thiocyanate ions show any effect. At pH<5.5 the presence of zinc leads to an extinction effect. This effect is strongly dependent on pH, and this is a drawback since during quantitative determination the pH has to be rigidly controlled. At pH<4.2 the main reagent—thiocyanate—gives the same effect, even in the absence of zinc (Curve 2). There is a short pH range with an optimum at 4.2-4.6 (Curve 4) for sensitive quantitative determination.

An analogous relation between change in rhodamine C color and pH was established spectrophotometrically (Fig. 2).

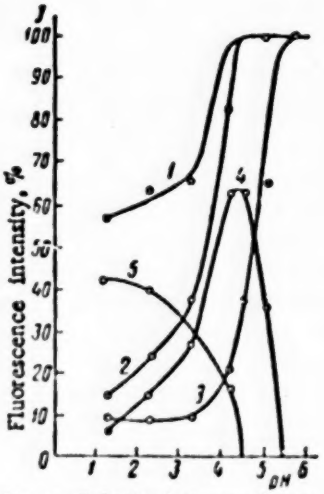

Fig. 1. Relation between fluorescence and pH in the system zinc thiocyanate-rhodamine C. 1) Fluorescence of rhodamine C; 2) ditto in the presence of thiocyanate; 3) ditto in the presence of thiocyanate and zinc; 4) the difference between the ordinates of curves 2 and 3; 5) difference between the ordinates of curves 1 and 2. $[Zn^{2+}]$ = [rhodamine] = 1.6×10^{-5}M; [KSCN] = 0.17M.

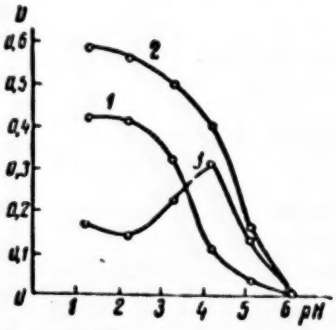

Fig. 2. Relation between optical density and pH in the system zinc thiocyanate-rhodamine C. 1) Optical density of rhodamine C in the presence of thiocyanate; 2) ditto in the presence of zinc; 3) the difference between ordinates of 2 and 3.

Optical density was measured on a SF-4 spectrophotometer at $\lambda = 590$ mμ and $l = 10$ mm. The concentration of all the components was the same as during measurement of the fluorescence (see Fig. 2). A 0.5% freshly prepared solution of gelatin was added as stabilizer.

The relation between the fluorescence extinction of rhodamine C and thiocyanate concentration is shown in Fig. 3*. A red filter was used during fluorescence measurements, and the fluorescence standard was a 2×10^{-5}M solution of rhodamine C; the fluorescence of this solution was taken as 100%. The suitable thiocyanate concentration range was found to be 0.05-0.2 M with an optimum at 0.08-0.1 M (Curve 1). At [KSCN] < 0.05 M no extinction was observed, while at [KSCN] > 0.2 M, extinction was observed even in the absence of zinc.

The pH of 5 and the thiocyanate concentration [KSCN] of 0.17 M recommended in the literature are within the pH and thiocyanate concentration limits we established, although they are not the optimum values [3, 4].

In order to study the relation between the fluorescence extinction of aqueous rhodamine C solutions and zinc concentration, solutions were prepared by the method given for photometric determination of zinc [3]. The only difference was that the final volume we used was 6 ml (instead of 60 ml) while the amounts of all reagents were correspondingly decreased. The fluorescence intensity of solutions with varying zinc contents was measured using a red filter; the fluorescence standard was the solution in the blank test; its fluorescence was taken as 100%. The experimental results are given in Fig. 4.

As Fig. 4 shows, it is possible to determine zinc quantitatively by measuring the fluorescence extinction of an aqueous solution of rhodamine C. Over the zinc concentration range 1-4 μg Zn in 6 ml, the fluorescence extinction is linearly proportional to zinc concentration. When the zinc content increases from 4-10 μg the color of the fluorescence changes from orange to red, and differences in the fluorescence intensity of the solutions decrease. The reproducibility of the results is 2%. The sensitivity of a determination is 0.08 μg zinc in 1 ml.

The basic characteristics of the fluorescent and photometric methods [3] obtained on the basis of a series of zinc determinations are given in the table.

The absorption curves of the reagent and of the colored zinc compound, taken on an SF-4 spectrophotometer at $l = 10$ mm, are shown in Fig. 5.

It is clear from Fig. 5** that even when excess zinc is present the total (integral) light absorption changes by 5% in all; the second maximum is weakly expressed and the color change is not large enough. It is best to use a spectrophotometer, the optical density being measured at 590-600 mμ.

*The thiocyanate concentration is plotted on a log scale.

**Results which have been published [3] were obtained during measurements on an FM photometer of the Pulfrich type using light filters, which essentially distort the actual relation of the absorption curves.

The decrease in fluorescence intensity of a solution, even in the presence of excess reagent (at a zinc content of 10 μg; see Fig. 4), amounts to 83%; this determines the high sensitivity of the fluorescent method of determination.

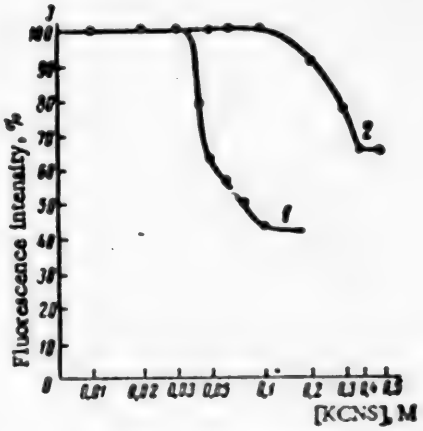

Fig. 3. Fluorescence of rhodamine C as a function of thiocyanate concentration. 1) In the presence of zinc; 2) without zinc. $[Zn^{2+}] = [\text{rhodamine}] = 2 \times 10^{-5}$ M; pH 4.7.

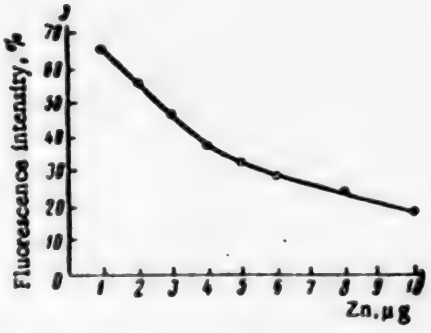

Fig. 4. Relation between the extinction of an aqueous solution of rhodamine C and zinc concentration.

The molar extinction coefficient calculated on the basis of published results on the composition of the zinc compound [2] and on the basis of our experimental results amounts to $6 \cdot 10^{-4}$ at λ_{559}. The disagreement between our results and published results ($E = 4.6 \cdot 10^{-4}$) is explained by the fact that we calculated the molar extinction coefficient for $\lambda_{max} = 590$ mμ (for the colored zinc compound), while the authors in [2] determined this value on an FÉK-M instrument fitted with a red filter, i.e., outside the region of maximum absorption of the colored zinc compound.

Basic Characteristics of the Fluorescent and Photometric Methods of Determining Zinc

Characteristics	Methods of determining zinc	
	Fluorescent	Photometric
Sensitivity	0.08 μg in 1 ml	0.13 μg in 1 ml
Relative experimental error	8-10%	15-25%
Concentration range over which determination is carried out	0.5-10 μg in 6 ml	8-25 μg in 60 ml
Final volume in the determination	6 ml	60 ml
Stability with time (optical density, fluorescence)	Does not change	For zinc contents of 25-15 μg in 60 ml, 30 min; 15 μg in 60 ml, 2.5 hr
Measurement time (of optical density, fluorescence)	Independent	One hour after pouring solutions together

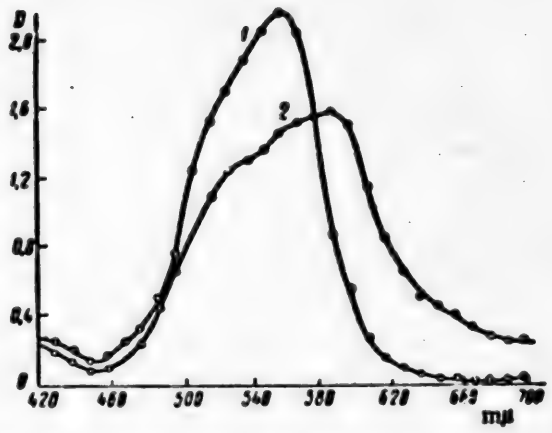

Fig. 5. Absorption curves of solutions of reagent and of the colored zinc compound. 1) Rhodamine C in the presence of thiocyanate. Rhodamine concentration = $5 \cdot 10^{-5}$ M; [KSCN] = 0.2 M; 2) Colored zinc compound. $[Zn^{2+}] = 3 \cdot 10^{-5}$ M.

SUMMARY

A comparative study has been made of photometric and fluorescent methods of determining zinc with rhodamine C. It has been shown that the most effective way of using formation of the zinc thiocyanate-rhodamine compound for zinc determination is to measure the fluorescence extinction of its solutions. The sensitivity of the method is 0.08 μg Zn in 1 ml.

The pH of the solutions is the most important factor which affects the color and the fluorescence. At pH>6, rhodamine C forms a pseudo base which does not react with either zinc or thiocyanate; at pH<4.2 thiocyanate ions form a colored and nonfluorescent compound similar to that formed by the zinc thiocyanate complex.

It has been established that the optimum pH and thiocyanate concentrations are about 4.2 and 0.1 M respectively.

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DETERMINATION OF CESIUM IN ROCKS BY A FLAME SPECTROPHOTOMETRIC METHOD

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Isotope dilution [1,2] and neutron activation methods [3] are used for the determination of cesium in rocks and meteorites. These methods are fairly sensitive and completely reliable, but the requisite apparatus is expensive and not readily available—factors which limit their possibilities for solving geochemical problems. Consequently cesium is often determined by the comparatively less sensitive, but more readily available and readily carried out spectrographic methods. Fabrikova's published method [4] on flame photometric determination of hundredths and thousandths of a percent of cesium in minerals cannot be applied to the determination of 10^{-4}% Cs in rocks.

Determination of cesium at the hundredths and thousandths percent level can be carried out by a technique developed for rubidium [5,6] after chemical treatment. The method satisfies the requirements of geochemistry both from the point of view of sensitivity and accuracy.

Cesium was determined on an apparatus consisting of a monochromator and photomultiplier using an air-acetylene burner [5]. Potassium and rubidium strongly supress cesium emission. Nevertheless, at a relatively high potassium and rubidium content (at concentrations K/Cs≥1500-2000) the cesium emission is almost constant (Fig. 1). The ratio K/Cs in various rocks is usually somewhat greater than the ratio indicated, so that there is no need to add potassium to test samples in order to get the necessary sensitivity, as indicated already [4]. Large amounts of potassium and rubidium present in samples and standards create a high background which even at narrow monochromator slit widths is often considerably higher than the cesium emission. The accuracy with which the background is measured in such cases is strongly reflected in the accuracy with which cesium is determined, this being particularly true when a monochromator with low dispersion is used.*

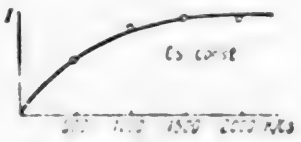

Fig. 1. Effect of potassium on cesium emission.

It is known that the background, which is determined by the lines of the elements which are located close to the test line, falls off exponentially, not linearly, and that in the case of a line with high intensity it leads to a certain error if the mean arithmetic value of the background is calculated from measurements made on both sides of the analytical line. In order to calculate the background more accurately we adopted the technique of measuring the background at three points for a standard solution not containing cesium; on this basis we calculated the value of the background in the test solution from the relationships $I^0_{b_1}/I^0_{b\lambda} = I^x_{b_1}/I^x_{b\lambda}$ and $I^x_{b_2}/I^0_{b\lambda} = I^x_{b_2}/I^x_{b\lambda}$ (where b = background) and not from their sum (see Fig. 2).** The method cannot be used when the intensity of cesium emission is considerably less than the background intensity when a monochromator of low dispersion is used. Preliminary chemical treatment is readily carried out [7].

Analytical Procedure. A one-g aliquot of finely ground silicate rock is moistened in a platinum basin with distilled water; 20-25 ml of hydrofluoric acid and 1 ml of sulfuric acid are added and the mixture carefully heated on a hot-plate until white fumes appear. The contents of the basin are stirred from time to time with a platinum spatula. When necessary, some more hydrofluoric acid is added. After evaporation to remove fluorides completely, a few

*We also used an ISP-51 spectrograph provided with an outlet slit for determination of cesium in rocks. Here the background value decreased strongly; the mean value of the background was calculated as the mean arithmetic value of the background on both sides of the line.

**A recording of part of the spectrum taken from Poluektov's book is reproduced in Fig. 2 [9].

drops of water are added and the contents of the basin again evaporated to dryness. The dry residue is calcined in the basin over a gas burner to a pale red incandescence for 1-2 min, as a result of which iron, aluminum, and some of the magnesium and calcium are converted to their oxides. To the cooled residue is added 50-70 ml of water, 0.5 g of ammonium carbonate, and 1-2 drops of concentrated ammonia solution. The mixture is transferred without filtration into a standard flask (100 ml), its volume made up to the mark, and after standing for 30-40 min filtered. An aliquot (80 from 100 ml of 160-170 ml from 200) is collected in a beaker and evaporated to dryness with nitric acid to remove ammonium salts. The alkali metal salts in the residue are dissolved in a small volume of water and the solution transferred to a standard flask or to a calibrated test tube. To this same flask is added methanol or ethanol until the alcohol concentration is 40% in order to increase the evaporation of the solution (this increases the sensitivity 2-2.5 times). The sodium, potassium, and rubidium contents are established before determining cesium. Samples are classified into several groups with differing potassium and rubidium contents (the potassium content is of basic importance); usually two or three groups are sufficient, with a potassium content of less than 1% in group I, 1-4% in group II, and 4-10% in group III. Standard solutions with approximately the same sodium, potassium, rubidium, and alcohol contents are prepared corresponding to each of these groups. The standard solutions contained the following amounts of cesium: 0.0; 0.1; 0.2; 0.5; 1.0; 1.5; 2.0; 3.0 μg/ml. Photometric measurements are made on the basis of the 852 mμ Cs line.

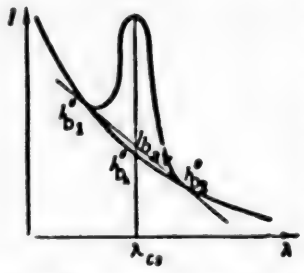

Fig. 2. Calculation of background value during cesium determination.

TABLE 1

Amount of Cs^{137} added cpm	Value of aliquot %	Activity of the aliquot, cpm	Cesium separated, %
1280	80	997	78
1280	85	1023	80
1280	87.5	1080	84.5

The completeness of separation of cesium by the method indicated was checked by adding known amounts of cesium 137 to a sample before decomposition. As the results in Table 1 show, the loss error does not exceed 5%.

The accuracy and reproducibility of the method was checked on synthetic solutions prepared from pure potassium, rubidium, and cesium salts (Table 2), and also by repeated cesium determinations on standard G-1 and several other samples (Table 3).

TABLE 2

Taken μg/ml			Cs found, μg/ml	Error, %
Cs	Rb	K		
0,12	10,0	980	0,11	−8,3
0,48	15,0	1960	0,50	+4,0
0,96	15,0	1960	0,99	+3,0
1,44	20,0	1960	1,39	−3,1
0,24	10,0	980	0,26	+8,3

TABLE 3

Sample	Found $n \cdot 10^{-4}$ %				Mean value	Published results [8]
G-1	2,2	2,0	1,8	2,1	$2,0 \cdot 10^{-4}$	$2,2 \cdot 10^{-4}$
	2,1	1,9				
Syenite No. 143	3,1	2,8	3,2	2,8	$3,0 \cdot 10^{-4}$	
	3,1					

The method has been used for determination of cesium in silicate rocks and also for the determination of 1×10^{-4} % to 7×10^{-4}% of rubidium in stone meteorites.

SUMMARY

A method is described for the determination of cesium in rocks; elements of the second and third groups are removed by chemical concentration. When instruments with low resolving power are used, it is recommended that the flame background be measured at three points using a solution free from cesium.

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RESEARCH IN THE ANALYTICAL CHEMISTRY OF THALLIUM

COMMUNICATION 6. NEW COMPLEXOMETRIC METHODS OF DETERMINING THALLIUM*

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The instability constant of the complex of trivalent thallium with sodium ethylenediaminetetraacetate (EDTA-Na) at 20° and at an ionic strength of 0.1 is $10^{-22.8 \pm 0.8}$ [1]. Accordingly it should be possible to carry out direct complexometric titration of Tl^{3+} at pH 2 using 1-(2-pyridylazo)-2-naphthol as indicator [2], and at pH 4-5 using xylenol orange [3]. Titration of Tl^{3+} at pH 2 posseses high selectivity; Cd, Zn, and Pb do not interfere. Fe^{3+}, Bi, Cu, Ni, and In interfere, as well as Cl^-, Br^-, and I^-; the latter three form complexes with Tl^{3+} at pH 2-3 which are more stable than those formed with the indicator**. Indirect methods which have been used are based on titrating excess EDTA-Na with standard solutions of Co^{2+} (indicator – SCN^-) [4], Th^{IV} (indicator–alizarin S) [5], Zn^{2+} (indicator–ferri-ferrocyanide mixture and benzidine) [6], V^V (indicator–diphenylcarbazide or diphenylcarbazone) [7], or on potentiometric titration with a Zn^{2+} salt using a Hg electrode as indicator [8]. In all the indirect methods described, titration was carried out at pH 4.5-5.0; this leads to a drop in selectivity.

For Tl^{3+} determination we have adopted the technique of titrating excess EDTA-Na with a standard solution of ferric alum in the presence of sulfosalicylic acid at pH 2; this technique permits determination of Tl^{3+} in the presence of Cd^{2+}, Zn^{2+}, Pb^{2+} and ≤0.1 M Cl^-. This is a decisive advantage of the method compared with direct titration at pH 2. Br^- ions interfere at pH 2.

For determination of trivalent thallium, 2 N NH_4OH solution is added to the test solution until a turbidity of $Tl(OH)_3$ appears; the latter is dissolved by addition of a few drops of concentrated HCl; 10 ml of standard EDTA solution is added, followed by five drops of 20% sulfosalicylic acid solution; the liquid is heated to 40-60° and titrated with a standard solution of $Fe(NH_4)(SO_4)_2$ until the yellow-green color of iron EDTA changes to an orange-red color (the result of the superposition of the red-brown color of iron sulfosalicylate on the yellow-green color) which does not disappear in the course of of one minute. Results are given in Table 1. Bi, In, Fe, and Cu interfere.

Separate determination of trivalent iron and thallium is based on the following. Trivalent thallium ions at pH 3 form a more stable complex with Br^- ions than with EDTA-Na. Br^- ions accordingly permit Tl^{3+} to be masked at pH 2. Under these conditions Fe^{3+} reacts with EDTA-Na quantitatively. After titration of Fe^{3+} ions at pH 2 in the presence of Br^- using sulfosalicylic acid as indicator, the pH of the solution is adjusted to 4-5 and trivalent thallium titrated using 1-(2-pyridylazo)-2-naphthol (or pyridylazoresorcinol) as indicated.

To the solution containing Fe^{3+} and Tl^{3+} is added 5-10 ml of 2 M KBr; NH_4OH is then added until the pH is 2; the liquid is heated to 40-60° and trivalent iron titrated with EDTA-Na solution until the red-brown color disappears. By adding CH_3COONH_4 the pH is adjusted to 4-5; a few drops of 0.1% pyridylazoresorcinol are added until a distinct red color*** shows; the trivalent thallium is then titrated with EDTA-Na solution until the color of the solution

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*Communication 5, see Zh. analit. khimii 15, 573 (1960).

**Halide ions do not interfere at pH 4-5, but the selectivity of the method with respect to the cations decreases sharply.

*** So that the rose color of the complex of Tl^{3+} with the indicator shows up more clearly against the yellow colored background arising from the iron EDTA complex, excess of the indicator must be added; accordingly, taking into account the limited solubility of 1-(2-pyridylazo)-2-naphthol in water, it is best to use water-soluble pyridylazoresorcinol.

changes to orange-yellow. A distinct color change is only observed when the iron content is not too high. At Fe^{3+} concentrations not exceeding that of Tl^{3+}, both titrations can be carried out with the same EDTA-Na solution: at higher Fe^{3+} concentrations the EDTA-Na solution used for the first titration should be more concentrated. The method for separate complexometric titration of trivalent iron and thallium gives satisfactory results (Table 2).

TABLE 1. Indirect Determination of Trivalent Thallium

Tl taken, mg	0.01169 M $Fe(NH_4)(SO_4)_2$ used, ml	Tl found, mg	Error, mg	Tl taken, mg	0.01169 M $Fe(NH_4)(SO_4)_2$ used, ml	Tl found, mg	Error, mg
12.61	3.28	12.52	—0.09	3.78	6.88	3.92	+0.14
12.61	3.25	12.60	—0.01	3.78	6.95	3.75	—0.03
12.61	3.22	12.66	+0.05	2.52	7.48	2.48	—0.04
6.30	5.95	6.14	—0.16	2.52	7.45	2.55	+0.03
6.30	5.90	6.26	—0.04				

TABLE 2. Separate Determination of Trivalent Iron and Thallium in Each Others Presence

Taken, mg		EDTA-Na solution used, ml		Found, mg		Taken, mg		EDTA-Na solution used, ml		Found, mg	
Fe	Tl	Fe	Tl	Fe	Tl	Fe	Tl	Fe	Tl	Fe	Tl
1.31	6.30	2.35*	3.00	1.31	6.11	20.40	6.30	3.20**	3.10	20.33	6.30
2.61	6.30	4.70*	3.05	2.62	6.21	20.40	6.30	3.25**	3.15	20.55	6.41
3.92	6.30	6.99*	3.15	3.89	6.41	20.85	6.30	6.45**	3.18	40.80	6.47
3.27	5.67	5.80*	2.84	3.36	5.78	20.80	3.15	6.48**	1.50	40.98	3.06

* EDTA-Na solution 0.009965 M, same for Fe and Tl.

** EDTA-Na solution 0.1132 M.

TABLE 3. Separate Determination of Trivalent Bismuth and Thallium in Each Others Presence

Taken, mg		Solution used, ml		Found, mg		Taken, mg		Solution used, ml		Found, mg	
Bi	Tl	0.1132 M EDTA-Na	0.0132 M $Cu(NO_3)_2$	Bi	Tl	Bi	Tl	0.1132 M EDTA-Na	0.0132 M $Cu(NO_3)_2$	Bi	Tl
39.0	6.30	1.98	2.98	38.8	6.40	39.0	12.61	2.13	5.85	37.6	12.58
78.0	6.30	3.58	2.95	78.3	6.34	97.5	6.30	4.35	2.90	96.5	6.23
19.5	6.30	1.10	2.95	19.6	6.34	97.5	2.52	4.15	1.10	95.5	2.36
19.5	12.61	1.35	5.90	19.2	12.69						

Successive determination of Cu^{2+} and Tl^{3+} is not feasible, since at pH 2, Tl^{3+} is titrated together with Cu^{2+} in the presence of Br^-; this is related to the smaller difference in the stabilities of their complexonates under these conditions. Successive titration of Bi^{3+} and Tl^{3+} is also impossible since BiOBr is precipitated in the presence of Br^- at pH 1.5-2. The following technique has been used for the separate determination of trivalent bismuth and thallium. Total Bi^{3+} and Tl^{3+} are titrated at pH 4-5 in the presence of 1-(2-pyridylazo)-2-naphthol or pyridylazoresorcinol; Tl^{3+} is then reduced to Tl^+ by means of Na_2SO_3 and the EDTA-Na thereby liberated titrated with standard $Cu(NO_3)_2$ solution.

To the test solution containing Bi^{3+} and Tl^{3+} is added dry ammonium acetate until the pH is 4-5 (the solution should remain clear), then a few drops of 0.1% methanol solution of 1-(2-pyridylazo)-2-naphthol and the resultant solution is titrated with EDTA-Na solution until the indicator color changes to yellow; about 0.1 g Na_2SO_3 is added, followed by some more indicator and the solution titrated with $Cu(NO_3)_2$ solution until the color of the solution changes from yellow to red-violet. Satisfactory results were obtained in this way, particularly for high amounts of thallium

The end point during direct complexometric titration of trivalent thallium can be established by making use of the interaction of the iodide complexes of trivalent thallium with EDTA-Na. As our experiments showed, the iodide complexes of trivalent thallium are so stable that at pH <6 they do not react with EDTA-Na, while at pH 6-8 this reaction proceeds quantitatively. Starch can be used as indicator (taking into account the specific characteristics of the iodide complexes of trivalent thallium) [9]: while trivalent thallium not bound as the complexonate is present in solution, i.e., TlI_4^- ions exist in the presence of I^-, then I_3^- ions will also be present at which color the starch blue; the blue color disappears at the end point.

To the test solution (3-30 mg Tl in 80-100 ml) is added several ml of 1 M tartaric acid; NH_4OH is then added until the color of the tropeoline 000 added changes from yellow-orange to rose; 1 M tartaric acid solution is next added until the yellow-orange color appears, and 1 ml of 1% KI is added (a yellow color, not rose, should appear at this stage; the rose color appears when the amount of KI added is not sufficient for formation of I_3^-; in such a case it is necessary to add a little more KI, a large excess being avoided because of the possibility of liberation of TlI). The final solution is titrated with EDTA-Na until the color changes from intense yellow to pale yellow; a few ml of 1% starch solution is added and titration continued until the blue color disappears. The method gives satisfactory results and possesses satisfactory reproducibility (Table 4).

TABLE 4. Complexometric Determination of Trivalent Thallium in the Presence of Starch-Iodide Indicator

Thallium, mg		Error		pH on completion of titration	Thallium, mg		Error		pH on completion of titration
taken	found	mg	%		taken	found	mg	%	
3,15	3,15	0	0	7,6	12,61	12,61	0	0	7,3
3,15	3,26	+0,11	+3,5	7,6	12,61	12,01	−0,60	−5	8,2
5,04	5,39	+0,35	+7	5,2	25,22	25,35	+0,13	+0,5	7,5
5,04	5,25	+0,21	+4	5,7	25,22	25,22	0	0	7,5
5,04	5,09	+0,05	+1	7,3	31,52	31,67	+0,15	+0,5	7,8
12,61	12,73	+0,12	+0,9	7,6					

At pH >8 low results are obtained, while at pH <6 high results are obtained. The method is not selective and many elements interfere.

SUMMARY

A method has been developed for the indirect complexometric determination of thallium at pH 2. The possibility has been demonstrated of carrying out successive complexometric titration of trivalent iron and thallium, and of bismuth and thallium. It has been established that the iodide complexes of trivalent thallium react stoichiometrically with EDTA-Na at pH 6-8, so that it has been possible to develop a complexometric method for determining thallium with a starch-iodide indicator.

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QUANTITATIVE DETERMINATION OF SCANDIUM BY MEANS OF HALOGEN-SUBSTITUTED MANDELIC ACID

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In a previous communication [1] we suggested a new method for determining scandium by means of mandelic acid; the scandium mandelate precipitate, however, has a comparatively high solubility in water. It was of considerable interest therefore to study halogen substituted mandelic acid as a precipitant for scandium. The introduction of electrophilic groups into an aromatic nucleus is known to lead to an increase in the sensitivity of precipitation; the introduction of halogens into the benzene ring increases the acid properties of the reagent and leads to a decrease in the solubility of the compounds formed with metals, and also to a decrease in the solubility of the reagent itself in water. It has been found that p-halogenomandelic acids quantitatively precipitate scandium from moderately acid solution, and that the solubility of the compound decreases with increasing molecular weight of the reagents.

EXPERIMENTAL

Reagents Used. Para-chloro-, p-bromo-, and p-iodomandelic acids were studied in the course of the work described here as precipitants for scandium. Apart from bromomandelic acid, we synthesized the reagents by Klingenberg's method [2]. By recrystallization from benzene it is possible to obtain pure preparations with m.p. 118-119° for p-iodomandelic acid. The values which we found for the solubility of the reagents in water at 20° are given in Table 1.

Study of Precipitation of Scandium with p-Halogenomandelic Acids. In order to establish the optimum conditions for precipitating scandium we studied the effect of the amount of the reagents and of the pH of the solution by a method described earlier [1]. It was found that considerably less of the p-halogenomandelic acids is required for complete precipitation of scandium than is the case when mandelic acid is used. Usually a concentration of 0.02 M p-chloro- or p-bromomandelic acid, and not more than 0.01 M p-iodomandelic acid, is enough to ensure precipitation.

TABLE 1. Solubility of Mandelic Acid and Its Halogenated Derivatives in Water at 20°

Acid	Solubility in water	
	moles per liter	g/liter
Mandelic Acid*	1.0	160.0
p-Fluoromandelic acid*	0.57	97.0
p-Chloromandelic acid	0.12	20.4
p-Bromomandelic acid	0.11	25.4
p-Iodomandelic acid	0.022	6.2

*The results on the solubility of mandelic acid and p-fluoromandelic acid determined by Belcher et al. have been included for comparison [3].

It is clear from Fig. 1 that scandium is precipitated in the acid range by p-chloro- and p-bromomandelic acids in the same way as by mandelic acid. Complete precipitation of scandium iodomandelate occurs at pH about 1 and higher; in the alkaline range, however, the interaction products of scandium with the given acids strongly differ from scandium mandelate.

Scandium mandelate is readily soluble in ammonia, forming $(NH_4)_3[Sc(C_8H_6O_3)_3]$, so that at pH > 3.2 scandium is not precipitated completely. The compounds of scandium with p-chloro- and p-bromomandelic acid are also soluble in alkaline media, but more sparingly soluble than scandium mandelate. The chloromandelate starts to dissolve at pH 4.0, while the bromomandelate starts to dissolve at pH 5. Moreover, on boiling these alkali solutions, rapid hydrolysis of the compound is observed with partial precipitation of the hydroxide or basic salts of scandium. Scandium iodomandelate, which does not form a similarly soluble complex compound, hydrolyzes when subjected to the effect of ammonia, and all the precipitate is converted into scandium hydroxide. It follows from these observations that the introduction of a halogen into the benzene ring of mandelic acid leads to a decrease in the stability of the complex compounds of scandium in an alkaline medium.

Next we determined the composition of the compounds isolated from acid media and washed with ether and ethanol. Scandium was determined by calcining the compound dried at 110° to the oxide, while the organic part was determined by cerimetric titration according to a method described by Verma [4,5]. The water of crystallization content was determined by difference and was also confirmed thermogravimetrically. The composition of the compounds (Table 2) is in good agreement with the formula $H_3[Sc(Hal \cdot C_8H_6O_3)_3] \cdot H_2O$, where Hal = Cl, Br, I.

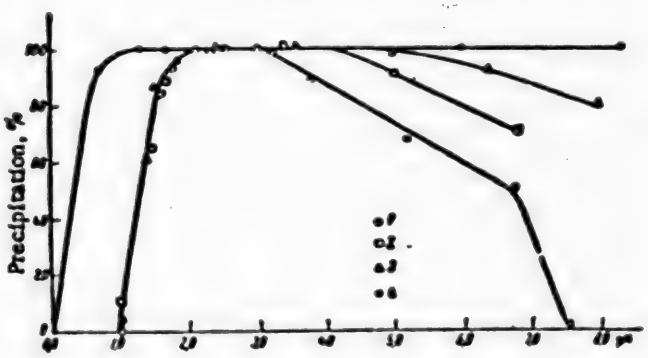

Fig. 1. Completeness of precipitation of scandium by mandelic acid and its halogeno derivatives as a function of the pH of the solutions. -o-o- scandium mandelate; -□-□- scandium chloromandelate; -Δ- scandium bromomandelate; -●-●- scandium iodomandelate.

Thermogravigrams of scandium halogenomandelates (Fig. 2) show that crystallization water contained in the compounds is removed at 120-160°. Decomposition of the compound starts at 260-280°, while over the range 500 to 540° the compounds are converted to scandium oxide.

For determination of the solubility of the series of compounds of scandium with mandelic acid and its halogeno derivatives, the precipitates obtained were washed with ether and ethanol, dried at 110°, placed in flasks and then shaken for about 40 hr at 20° until equilibrium was reached. The precipitates were filtered off at the end of this period and scandium determined photometrically in a known volume of the filtrates. Results for the solubility of scandium mandelate and halogenomandelates in water are given in Table 3.

TABLE 2. Results of Analyses of the Compounds

Compound	Sc, %		Hal · $C_8H_6O_3$, %		H_2O, %	
	calculated	found	calculated	found	calculated	found
$H_3[Sc(Cl \cdot C_8H_5O_3)_3] \cdot H_2O$	7,47	7,42	89,63	89,92	2,99	2,66
$H_3[Sc(Br \cdot C_8H_5O_3)_3] \cdot H_2O$	5,97	6,06	91,63	91,85	2,40	2,11
$H_3[Sc(I \cdot C_8H_5O_3)_3] \cdot H_2O$	5,03	4,87	92,86	93,26	2,01	1,87

Determination of Scandium in Solutions of Its Salts and in the Presence of the Rare Earths. Results for determination of scandium by means of p-halogenomandelic acids are given in Table 4. The methods permit determination of milligram amounts of scandium in 100 ml of solution.

TABLE 3. Solubility of Scandium Mandelate and Halogenomandelates in Water at 20°

Compound	Solubility in water	
	moles per liter	g/liter
Scandium mandelate	$8.8 \cdot 10^{-5}$	0.03986
Scandium chloromandelate	$1.6 \cdot 10^{-5}$	0.00896
Scandium bromomandelate	$1.3 \cdot 10^{-5}$	0.00904
Scandium iodomandelate	$6.5 \cdot 10^{-6}$	0.00537

The rare earths are precipitated by these acids at high pH values. For example, the chloro- and bromomandelates of the rare earth elements of the cerium group are precipitated at pH values higher than 3.5, while the iodomandelates of these elements are precipitated at pH about 2.5. These reagents therefore permit separation of scandium from the rare earths.

As an example we have studied in detail the possibility of determining scandium in the presence of cerium group rare earths by means of p-bromomandelic acid. Experiments showed that the rare earths are partially coprecipitated with scandium when only one precipitation is carried out; reprecipitation is therefore necessary.

Thorium should be absent since it is also precipitated by the reagents under indentical conditions; thorium can however be complexed with citric acid. Table 5 contains results for the separation of scandium from cerium group rare earths.

Extraction of the Compounds with Organic Solvents. Scandium mandelate is insoluble in common solvents, and it only floats in some of them. The introduction of halogens into the benzene ring of mandelic acid, particularly introduction of chlorine and bromine, leads, however, to an increase in the extractability of the complex compounds. Scandium chloro- and bromomandelates are readily extracted by several oxygen-containing solvents, e.g., n-butanol, isoamyl alcohol, cyclohexanone, ethyl acetate, and other alcohols, ketones, and esters. They are insoluble, however, in ethyl ether, methanol, ethanol, benzene, chloroform, carbon tetrachloride, etc. Scandium iodomandelate floats and is not extracted by these solvents.

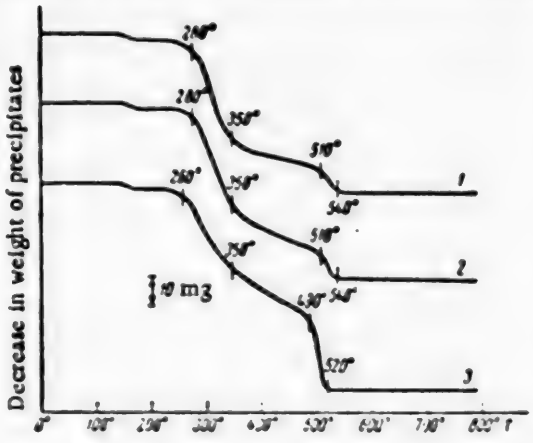

Fig. 2. Thermogravigrams. 1) Scandium chloromandelate; 2) scandium bromomandelate; 3) scandium iodomandelate.

We have studied the extraction of scandium chloro- and bromomandelates with isoamyl alcohol. 98-100% of the scandium compound passes into the organic phase in one extraction. Extraction experiments were carried out as follows. To a solution (for example 10-20 ml) containing scandium (5-100 μg) we added hydrochloric acid or ammonia to control the pH. Scandium was then extracted with a 0.01 M solution of p-chloro- or p-bromomandelic acid in isoamyl alcohol, the volume of which was the same as that of the aqueous phase. After the phases had separated out, scandium was determined photometrically in both the aqueous and organic phases. The scandium in the organic phase was reextracted with 1 N hydrochloric acid. Fig. 3 shows the relation between the extraction of the chloro- and bromomandelates of scandium and the cerium group rare earths and the pH of the solution; it follows from Fig. 3 that by using an extraction method it is possible to extract microamounts of scandium, and to separate it from large amounts of the rare earths. Table 6 contains results on the separation of scandium from cerium-group rare earths by extraction of the bromomandelates with isoamyl alcohol at pH 3.0-3.5.

TABLE 4. Determination of Scandium in a Solution of its Salt by means of p-Halogenomandelic Acids

Reagent	Sc_2O_3, mg		Error, %
	taken	found	
Cl—C_6H_4CH(OH)·COOH	0,98	1,00	+0,02
	4,93	4,94	+0,01
	9,86	9,85	—0,01
Br—C_6H_4—CH(OH)·COOH	1,01	1,02	+0,01
	3,03	3,03	±0,00
	10,10	10,10	±0,00
I—C_6H_4—CH(OH)—COOH	0,98	0,96	—0,02
	4,93	4,95	+0,02
	9,86	9,88	+0,02

TABLE 5. Determination of Scandium in the Presence of Cerium Group Rare Earths by Means of p-Bromomandelic Acid

Sc_2O_3, mg		Ratio Sc_2O_3 : (total rare earths)$_2O_3$	No. of precipitations	Error, mg	Sc_2O_3, mg		Ratio Sc_2O_3 : (total rare earths)$_2O_3$	No. of precipitations	Error, mg
taken	found				taken	found			
3,03	3,98	1 : 1	1	+0,95	2,02	2,10	1 : 10	2	+0,08
3,03	3,00	1 : 1	2	—0,03	3,03	2,99	1 : 10	2	—0,04
10,10	10,02	1 : 1	2	—0,08	1,01	1,08	1 : 50	2	+0,07
10,10	10,15	1 : 1	2	+0,05	1,01	0,96	1 : 100	2	—0,05

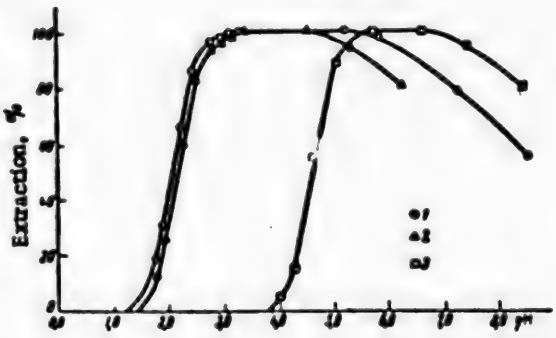

Fig. 3. Relation between extraction of halogenomandelates of scandium and of the cerium group rare earths and the pH of the aqueous phase. -o-o- Scandium bromomandelate; -Δ-Δ- scandium chloromandelate; -□-□- bromomandelates of cerium group rare earths.

SUMMARY

Precipitation of scandium with p-halogenomandelic acids has been studied. The composition of the precipitates formed corresponds to the formula $H_3[Sc(Hal \cdot C_8H_6O_3)_3] \cdot H_2O$ (where Hal = Cl, Br, I).

Methods have been developed for the determination and separation of scandium from cerium-group rare earths by means of p-halogenomandelic acids.

Extraction of scandium p-bromo- and p-chloromandelates with water-immiscible organic solvents has been studied, and it has been shown that scandium can be separated from cerium group rare earths by extraction with isoamyl alcohol.

TABLE 6. Separation of Scandium from Cerium Group Rare Earths by Extraction

Sc_2O_3, μg		Ratio Sc_2O_3 : : (total rare earths)$_2O_3$	Error, μg	Sc_2O_3, μg		Ratio Sc_2O_3 : : (total rare earths)$_2O_3$	Error, μg
taken	found			taken	found		
25,0	24,8	1 : 50	—0,2	10,0	10,0	1 : 2500	±0,0
25,0	24,5	1 : 50	—0,5	10,0	9,6	1 : 2500	—0,4
25,0	24,3	1 : 250	—0,7	10,0	9,6	1 : 5000	—0,4
25,0	25,3	1 : 250	+0,3	10,0	10,1	1 : 5000	+0,1
15,0	14,5	1 : 500	—0,5	5,0	5,1	1 : 5000	+0,1
15,0	15,0	1 : 500	±0,0	5,0	4,9	1 : 5000	—0,1
15,0	14,6	1 : 1000	—0,4	5,0	5,7	1 : 10000	+0,7
15,0	14,8	1 : 1000	—0,2	5,0	5,8	1 : 10000	+0,8

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

SPECTROGRAPHIC DETERMINATION OF GERMANIUM AND OTHER ELEMENTS IN ORES WITH SULFIDATION OF THE LATTER DURING THEIR EVAPORATION*

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Increasing the Sensitivity of the Determination of Elements during Sulfidation of Samples. The fractional evaporation effect is used very widely during spectrographic determination of small amounts of elements in ores, minerals, and other objects. When the rate of fractional distillation of compounds of the test elements is high enough, the concentration of their atoms in the cloud of the light source increases significantly, the intensity of the lines of the elements increases with respect to the background of the spectrum, and consequently the sensitivity of their determination increases.

The use of fractional evaporation of elements for increasing the sensitivity of their determination is only possible in some cases by effecting corresponding changes in the chemical composition of the test materials. This can be realized during the evaporation process in the spectrum excitation source by adding appropriate reagents to the test material [1-5]. The basic condition which decides the choice of reagent is that formation of readily volatile compound of the impurity elements should proceed sufficiently rapidly, while the elements present in large amounts in the test material should form compounds which are sparingly volatile compared with compounds of the impurity elements.

Our observations show that an appreciable increase in the sensitivity of determination is observed in many cases for elements which form readily volatile sulfides, on adding sulfur powder to test oxide and other ores, and evaporating the mixture of powders in a reducing medium from the electrode crater of a carbon arc used for spectrum excitation. Under such conditions, one would expect the greatest increase in sensitivity for those elements whose sulfide compounds differ sharply from their oxide compounds in their vaporizability.

In Fig. 1 is shown a comparison of the duration of evaporation of equal atomic amounts of elements when they are introduced into the crater of a carbon electrode in the form of their sulfides or oxides, in the absence of compounds of other elements. 1×10^{-4} g·atom of the respective elements was evaporated from the crater of a carbon electrode 3.5 mm in diameter and 5 mm deep. The arc was fed with an ac current of 8 amp, 220 v. The amount by weight of the evaporated compounds was varied in accordance with their molecular weight; the weights used varied from 5 to 25 mg.

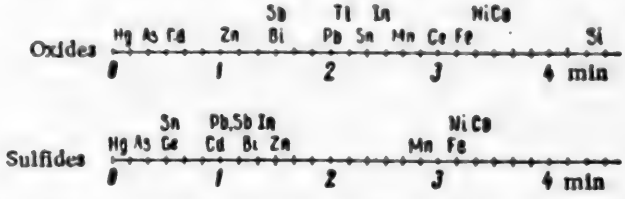

Fig. 1. Duration of evaporation of 1×10^{-4} g·atom of the elements in the form of their sulfides and oxides from the crater of an ac carbon electrode arc.

As Fig. 1 shows, on switching from the oxides to the corresponding sulfides a very significant increase in the rate of evaporation is observed in the case of germanium; the evaporation rate of lead sulfide and particularly of tin sul-

* Reported at the All-Union Conference on the Analysis of Rare and Semiconducting Elements, convened by GEOKhI, AN SSSR (Moscow, December 1959) and at the Conference on Spectrographic Analysis of Ores for Rare and Scattered Elements convened by the Ministry of Geology and Conservation of Mineral Resources of the USSR (Tashkent, April 1959).

fide also exceeds the evaporation rate of their oxides. No large differences are observed in the rate of evaporation of oxide and sulfide compounds of the remaining elements.

It should be noted that on switching from oxides to sulfides the change in evaporation conditions shown in Fig. 1 is only maintained in those cases where the elements are present in the test ore in the form of oxides, distributed as isolated mechanical impurities which react rapidly in a reducing medium with sulfur, and do not react with the main element of the sample to form new, sparingly volatile compounds. A significant increase in the sensitivity of determination is achieved on evaporating, in the presence of sulfur, quartz and silicate powders containing the oxide compounds of microelements which tend to form sulfides, the oxides being present as mechanical impurities.

In those cases where the elements to be determined are present in the form of isomorphous impurities, or, after fusion of the test sample, enter into the composition of the melts formed, the chemical composition of the melts affects their capacity to evaporate. In this connection therefore there may be a divergence from the changes in evaporation rate of the elements on going from oxides to sulfides shown in Fig. 1. Accordingly, in choosing reagents which modify the composition of the test sample during its evaporation, one must be guided not only by the capacity of the impurity elements to form readily volatile compounds in an isolated state, but also by the capacity of the melts of the freshly formed materials to retain the impurity elements.

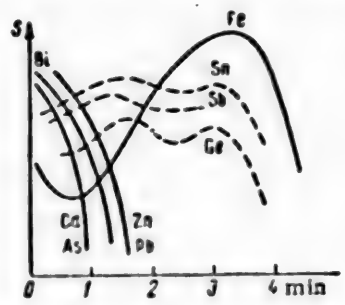

Fig. 2. Change in blackening of lines of impurity elements present as oxides during evaporation of iron oxide from a carbon electrode crater.

The effect of the composition of the melts on the evaporation rate of the elements is shown most often in those cases where the oxides are analyzed; consequently, sulfidation of oxide ores, whose melts in many cases retain the test elements fairly strongly, has undoubted practical importance. Thus during evaporation of iron oxide ores, the melts of the latter strongly retain germanium, tin, and antimony, and separate passage of these elements and iron into the arc cloud is impossible. The lines of germanium, tin, and antimony are observed together with those of iron in the spectrum of the arc cloud throughout evaporation of an iron ore from the electrode crater (Fig. 2).

The picture of the change in intensity of the lines of germanium, antimony, and tin is totally different when a mixture of iron oxides and sulfur in the proportion 2:1 is evaporated. Under these conditions germanium, tin, and antimony evaporate completely in 50-90 sec in the arc cloud from the melt of iron sulfides formed rapidly in the electrode crater.

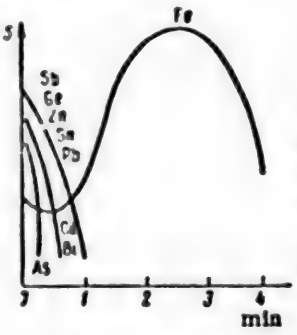

Fig. 3. Change in the blackening of lines of impurity elements present as oxides on evaporating a mixture of iron oxide and sulfur from a carbon electrode crater.

Under such conditions the iron mainly passes into the arc cloud only after complete evaporation of germanium, tin, and antimony; thus the iron background which is characteristic of the spectrum is absent on the spectrogram. A comparison of Figs. 2 and 3 shows that on adding sulfur to iron oxide ores, the time taken by lead, cadmium, zinc, and bismuth to pass into the arc cloud is also shortened; these elements evaporate during the initial burning stages of the arc. An examination of Figs. 4 and 5 indicates that addition of sulfur to quartz containing the oxides of impurity elements leads to rapid evaporation of chalcophilic elements in the arc flame.

In the absence of sulfur, part of the impurity elements present as oxides succeed in combining with the quartz before evaporation to form silicates, and when the melts are not heated strongly enough are firmly retained by the latter.

It should be borne in mind that the evaporation conditions indicated in Figs. 2-5 relate to the case where the arc is fed by an ac current, force-ignited by high-frequency currents; there is a spot in the arc at which there is less heating of the electrodes than in a dc arc or in the case of a free burning ac arc. Thus during evaporation of ores in a dc arc from the crater of a carbon anode the passage time of the elements is shortened, and it is possible to evaporate from silicate melts into the arc flame not only Hg, As, Pb, Cd, Bi, and Zn, but also Ge, Sn, and Sb if the arc is allowed to burn long enough.

In most cases, addition of sulfur to test ores containing large amounts of iron, quartz, and silicates leads to a significant increase in the sensitivity of the determination of elements which form volatile sulfides. Evaporation of about 20 mg of iron oxide ores in the presence of sulfur from the electrodes leads to an increase in the sensitivity of determination from $1 \times 10^{-3} - 7 \times 10^{-4}$ to 1×10^{-4}% in the case of germanium.

Increase in sensitivity depends to a large extent on the amount of sample placed in the electrode, since this amount determines the amount of microelements passing from the sample into the arc cloud. Accordingly, the highest sensitivity is achieved on evaporating the test samples from chamber electrodes heated independently, up to 10 g of test material being used [3, 6-9].

On evaporating 0.4 g of an iron oxide ore mixed with sulfur from chamber electrodes independently heated, it is possible to detect $1 \times 10^{-3} - 7 \times 10^{-6}$% of germanium on the basis of its 2651.2 A line. Under these conditions it is also possible to determine 1×10^{-5}% cadmium, thallium, tin, antimony, bismuth, arsenic, and zinc in iron oxide ores.

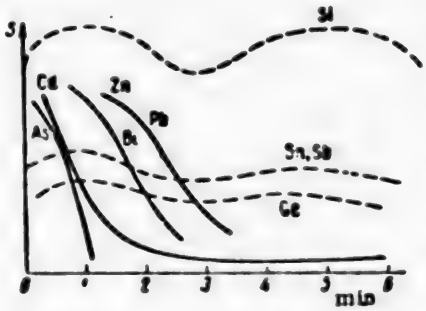

Fig. 4. Change in blackening of lines of impurity elements present as oxides on evaporating quartz from a carbon electrode crater.

On adding sulfur to the test sample a vigorous evaporation of sulfur in the arc flame occurs. The ionization potential of sulfur (10.4 ev) is lower than the effective ionization potential established in an arc cloud burning between spectrographically pure carbon electrodes; the appearance of sulfur, despite the fact that its ionization potential is high enough, leads during the initial stages of burning to a drop in flame temperature from 7400 to 4600°K. Subsequently the arc temperature increases rapidly as the sulfur evaporates.

The indicated change in flame temperature is stable in character, and only depends to a small extent on the composition of the test samples in those cases where the latter do not contain a large amount of elements which occur early on in the volatility series of the sulfides in a carbon arc [10].

Fig. 5. Change in blackening of lines of elements present as oxides on evaporating quartz mixed with sulfur from a carbon electrode crater.

It should also be pointed out that addition of sulfur to samples being evaporated determines to a large extent not only the way in which the flame temperature changes, but also the conditions for diffusion removal of the impurity elements from the arc cloud. Accordingly, addition of sulfur favors an increase in the reproducibility of the determination of trace elements passing simultaneously with sulfur into the arc cloud. Addition of sulfur also prevents sputtering of the sample, sputtering being frequently observed, e.g., during evaporation of iron oxide ores.

Quantitative Determination of Germanium in Iron Oxide and Sulfide Ores, Silicates, and Coal Ash. Most published methods for the quantitative determination of $1 \times 10^{-2} - 4 \times 10^{-4}$% germanium are based on evaporation of test ores and coal ash from the crater of a carbon electrode, from the surface of a rotating metallic electrode or from paper strips [12-21]. An article has been devoted to the determination of germanium in iron oxide ores [1] in which use is made of the increase in the germanium line with respect to the iron lines and to the spectrum background during the initial moments of evaporation of the ore. The incomplete evaporation of germanium observed in this case is determined by the relationship between the results and the composition of the test ore.

During the search for germanium in iron oxide ores a method which attracted attention was one which permitted determination of 4×10^{-4}% germanium; germanium determination was based on blowing the powdered ore into the cloud of a horizontally arranged ac arc [22]; using this blowing technique, incomplete evaporation of the germanium from the ore was again observed.

As noted earlier, conditions for complete and rapid evaporation of germanium are attained on sulfidation of iron oxide ores during their evaporation from the crater of a carbon electrode.

Additions to iron oxide ores of reagents ($SnCl_2$, $CuCl_2$) which are capable in a reducing medium of forming volatile germanium chlorides, and also addition of crystalline iodine, which gives volatile germanium iodides, as is evident from Figs. 6 and 7, do not give better results than those obtained when the germanium is evaporated from iron oxide ores by addition of sulfur. The characteristic way in which germanium passes into the arc cloud during evaporation of a mixture of an ore with iodine is determined by the fact that a considerable amount of germanium does not succeed in reacting with iodine, since the latter volatilizes very rapidly from the electrode crater.

Neither does germanium distill into the arc cloud with the requisite rapidity and completeness on adding various salts of the alkalimetals (KCl, KI, KIO_3 etc.) or on addition of potassium pyro-antimonate; these salts lower the temperature of the arc and the melt and favor distillation with them of the volatile compounds of the elements from the melt.

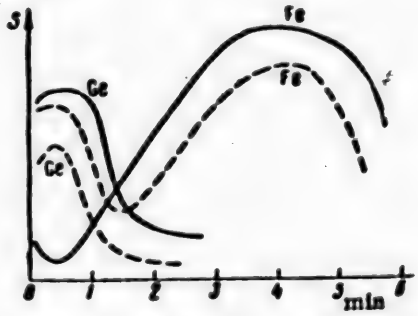

Fig. 6. Change in blackening of lines of impurity elements present as oxides during evaporation of iron oxide mixed with $SnCl_2$ and $CuCl_2$ from a carbon electrode crater. $SnCl_2$ —; $CuCl_2$ - - - .

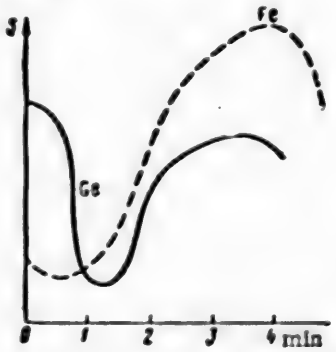

Fig. 7. Change in blackening of lines of impurity elements present as oxides during evaporation of iron oxide mixed with iodine from a carbon electrode crater.

Analytical Procedure. The test powder of iron oxide ore is mixed in the proportion of 2:1 with powder consisting of equal parts by weight of sulfur and quartz, and the whole ground in an agate mortar in the presence of alcohol. 0.5% of antimony oxide, which is used as an internal standard, is added beforehand to the powder, which is mixed with test ore. Sixty mg of the mixture of ore, sulfur, and quartz powder is introduced into the opening in a spectrographically pure carbon electrode. The diameter of the opening is 3.5 mm while its depth is 5 mm, and the wall thickness is 1 mm. This electrode is fixed at a distance of 3 mm below the upper electrode, which is a spectrographically pure carbon electrode sharpened to a cone. The electrodes are fixed by means of their shadow projections in a position which will ensure that during the first moments after the arc has been ignited the image obtained of the central part of the arc flame will fall on the diaphragm of the intermediate lens. The slit is illuminated by means of a three-lens illuminating system. The spectra are photographed with an ISP-28 quartz spectrograph "Spectrographic" Type 2 plates, with a sensitivity of 16 GOST units. The arc is fed with a current of 8 amp at 220v from a DG-2 ac arc generator.

The spectra are photographed in the course of the first 100 sec after the arc has been ignited; this time is sufficient for all the germanium to evaporate from the test sample.

Calibration curves constructed within the coordinates ΔS vs log C are used for calculating the germanium concentration of test samples. When the germanium concentrations in the samples are low (0.0001-0.0002%) the curves are constructed within the coordinates $\log(I/I_{\text{int. standard}})$ vs log C; the background intensity is subtracted from the line intensities.

Standard ore samples whose germanium contents have been established fairly accurately by chemical analysis are used for constructing the calibration curves. When no ore samples are available whose germanium contents have been established chemically, ore powders free from germanium can be taken and known weights of germanium dioxide added to them. Standard powders are prepared by successive dilution, 2-3 times, of a standard powder with a high germanium content with ore free from germanium. The dilution process should be accompanied each time be careful mixing and grinding of the powders in an agate mortar.

TABLE 1

Analytical lines	Concentration ranges over which germanium was determined, %	Lines of interfering elements	Control lines of interfering elements	Approximate concentration of interfering elements, %
Ge I 2651.18 and Sb 2670.64	0.0001–0.01	Pb bands 2647–2659	Zn 2682.8	>10 > 5
		Zn 2670.53		
Ge I 2651.18 and Sb I 2877.92	0.0001–0.01	Pb bands 2647–2659		>10
		Cr 2877.98	Cr 2875.99	>1

Table 1 contains the wave lengths of the analytical pairs of lines, the germanium concentration ranges determined, and the lines of elements which interfere with germanium determination.

Experience has shown that the technique suggested can be used for analyzing not only iron oxide ores but also iron sulfide ores, silicates, and coal ash.

When ores are converted into sulfides, the effect of comparatively sparing volatile foreign elements present in large amounts in the test sample decreases, and changes in the composition of the test sample over reasonable limits do not lead to the appearance of systematic errors. As an example, Fig. 8 illustrates the distribution of points on the curve constructed within the coordinates ΔS, log C for the case of the analysis of iron oxide and iron sulfide ores from different ore deposits, and for coal ash.

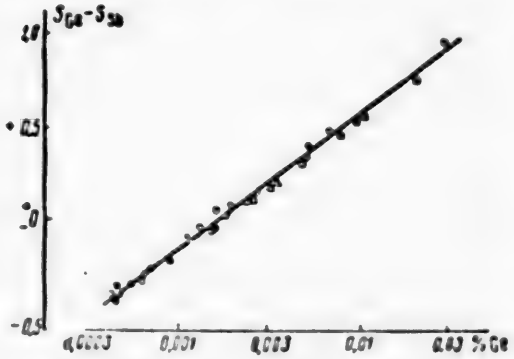

Fig. 8. Relation between difference in blackening of the lines Ge I 2651.18 and Sb 2670.64 and germanium concentration of a test sample. ● Iron oxide ore; o magnetic fraction; × martite ore; Δ polmetallic ore; □ coal ash.

Tables 2 and 3 contain as examples comparisons of the results of chemical and spectrographic analysis of oxide and sulfide ores and coal ash and also the results of spectrographic analysis of ore samples to which germanium has been added.

The probable error of a duplicate determination of germanium proved to be 6%. The error may increase 1.5-2 times in the case of the lowest germanium contents.

The technique indicated has been used over a long period for the analysis of iron oxide ores containing germanium. One spectroscopist in the course of a working day can analyze 15 ore samples for their germanium content.

As noted above the sensitivity of the determination of germanium in ores can be increased by using electrodes which can hold a larger amount of test sample. In such cases, however, the reproducibility in the values obtained for germanium is observed to fall off.

TABLE 2

Composition of sample	Ge, % spectrographically	Ge, % chemically	Ge, % mean	Error (relative), %
Iron ore	0,0052	0,0049	0,0050	+4
" "	0,00067	0,00066	0,000065	+3
" "	0,00085	0,0010	0,0009	−5,5
" "	0,0014	0,0017	0,0015	−6,5
Magnetic fraction	0,0020	0,0018	0,0019	+10
" "	0,0046	0,0050	0,0048	−4
" "	0,0068	0,0065	0,0066	+3
" "	0,0014	0,0012	0,0013	+4
" "	0,0006	0,0006	0,0006	±0
" "	0,00040	0,00045	0,00042	−4,5
Martite ore	0,00046	0,00050	0,00048	−4
" "	0,0012	0,0010	0,0011	+10
Hematite ore plus quartz	0,00040	0,00045	0,00042	−4,5
	0,00040	0,00045	0,00042	−4,5
Polymetallic ore	0,0032	0,0033	0,00325	−1,5
	0,0028	0,0035	0,0031	−10
Coal ash	0,030	0,026	0,028	+ 7
" "	0,009	0,010	0,0095	+5
" "	0,023	0,025	0,024	− 4
" "	0,0044	0,0045	0,00445	−10
" "	0,0070	0,0077	0,0073	− 4

TABLE 3

Composition of sample	Ge, % taken	Ge, % found	Error (relative) %
Iron ore	0,00028	0,00029	+3,6
" "	0,00028	0,00027	−3,6
" "	0,00028	0,00035	+25
" "	0,00055	0,00057	+3,6
" "	0,00055	0,00059	+7,3
" "	0,00055	0,00046	−16,3
" "	0,00055	0,00065	+18,2
Iron ore + 50% Al_2O_3	0,0013	0,0013	±0
Iron ore + 50% MnO_2	0,0013	0,0013	±0
Iron ore + 50% MgO	0,0013	0,0014	+8
Iron ore + 50% CaO	0,0013	0,0015	+16
Iron ore + 50% TiO_2	0,0013	0,0013	± 0
Iron ore + 50% SiO_2	0,0013	0,0011	−16
Iron ore + 50% of a mixture consisting of equal amounts of Al_2O_3, MnO_2, MgO, CaO, TiO_2, SiO_2	0,0013	0,0013	± 0

SUMMARY

A study has been made of the conditions under which chalcophilic elements pass into the arc cloud during evaporation of ores and silicates in the presence of sulfur.

A method is suggested for the analysis of oxide ores, coal ash, silicates, and other materials in which the test materials are subjected to sulfidation during their evaporation from the crater of a carbon electrode; this technique opens up possibilities of increasing the sensitivity, reproducibility, and accuracy of the determination of elements which form volatile sulfides.

Sulfidation of samples is particularly effective in the analysis of iron oxide ores, in which it is very difficult to determine low germanium contents.

When electrodes of the usual type containing 60 mg of a mixture of test sample and sulfur are used, it is possible to determine quantitatively 0.0002% of germanium in ores, silicates, and coal ash with an error of 10%; use of chamber electrodes capable of holding larger samples leads to a 10- to 20-fold increase in sensitivity.

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2-(4-CHLORO-2-PHOSPHOBENZENEAZO)-1,8-DIHYDROXYNAPHTHALENE-3,6-DISULFONIC ACID (CHLORPHOSPHONAZO I) AS A REAGENT FOR THE PHOTOMETRIC DETERMINATION OF SEXIVALENT URANIUM

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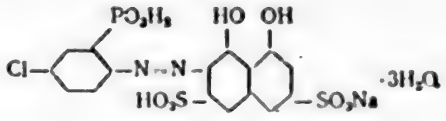
Reagents containing the arsono group [1-7] have found wide application for the photometric determination of uranium. Among these, azo derivatives of chromotropic acid with the arsono group in the position ortho to the azo group have proved particularly effective for this purpose; this is especially true of 2-(2-arsonobenzeneazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid, often called uranon or arsenazo [8,9].

Since phosphoric acid, which is similar in many respects to arsenic acid, forms more stable compounds with sexi- and quadrivalent uranium than does arsenic acid, it might be expected that the corresponding organic derivatives of phosphoric acid should also form more stable compounds with uranium. In this connection a study of the corresponding organic derivatives of phosphoric acid is of interest and worth carrying out.

The absence of published results on the use of colored organic reagents containing the atomic group PO_3H_2 for the photometric determination of a series of metals, including uranium, is a consequence of the fact that no methods are known for preparing the corresponding compounds. Several of these compounds are being synthesized at present by Lukin et al. [10]. The present article contains results of a study of 2-(4-chloro-2-phosphobenzeneazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid (which we have designated chlorphosphonazo I for short) as a reagent for the photometric determination of sexivalent uranium. The composition and structure of chlorphosphonazo I correspond to the formula:



Chlorphosphonazo I is very soluble in water; neutral and acid solutions have a red color, while alkaline solutions are violet. Weakly acid solutions of chlorphosphonazo have a maximum light absorption at 515 mμ (see Fig. 1, Curve 1). The position of the absorption maximum is independent of pH over the range 4.0-7.5 (see Fig. 2, Curve 1). On adding a number of metals to weakly acid solutions of chlorphosphonazo I the color of the solutions change from red to violet; in the case of sexivalent uranium to blue. Chlorphosphonazo I behaves in the same way as arsenazo, which also only forms a blue color with sexivalent uranium. The light absorption maximum of solutions of the compound of chlorphosphonazo I with sexivalent uranium occurs at 605 mμ (see Fig. 1, Curve 2); the molar extinction coefficient is 23,100; The molar extinction coefficient of the corresponding compound of sexivalent uranium with arsenazo is 22,800 [6], or 22,900 according to other results [4]. Thus the sensitivity with which uranium can be determined with chlorphosphonazo I is approximately the same as that when arsenazo is used.

A study of the relation between the light absorption of solutions of the compound of chlorphosphonazo I with sexivalent uranium and pH showed that the shape of the light absorption curves and the height of the maximum (Fig. 2 curve 2) hardly change at all over the range pH 5.2-8.0. The light absorption of solutions of the compound of uranium with chlorphosphonazo I, in contrast to that of solutions of the corresponding compound with arsenazo, is independent of the pH of the solutions over fairly wide limits; the value of the light absorption of the corresponding solutions of

the compound of sexivalent uranium with arsenazo is different for almost all pH values [4]. As a result of this, during determination of uranium by means of chlorphosphonazo I, small variations in acidity cannot lead to changes in light absorption, and for this reason do not affect the accuracy of uranium determination.

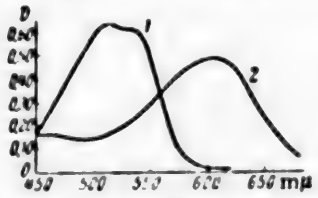


Fig. 1. Light absorption of solutions of chlorphosphonazo I and of its compound with sexivalent uranium as a function of wave length (SF-4 spectrophotometer; cuvette with layer thickness of 1 cm; optical density measured relative to water). 1) 2×10^{-5} M solution of chlorphosphonazo I, pH 6; 2) chlorphosphonazo I 2×10^{-5} M and $UO_2(NO_3)_2$ 3×10^{-5} M, pH 6.

Chlorphosphonazo, in contrast to arsenazo, permits determinations to be carried out in more acid solutions. This is another advantage, since on carrying out determinations at lower pH values, it is possible to diminish or completely avoid interference from a number of masking agents (tartrates, citrates, oxalates, ethylenediaminetetracetic acid).

Chlorphosphonazo interacts with sexivalent uranium in the molar proportion of 1:1 (Fig. 3). Similar results were obtained both by the isomolar series method, and by the method of varying the concentration of one of the components while that of the other component is kept constant. The sharp break on the curves indicates that the compound formed has a fairly high stability. On the basis of the results obtained, the instability constant, calculated on the basis of the isomolar series method [11] was found to be 4×10^{-8}; this is greater than the corresponding value for the arsenazo compound, which is 5×10^{-8} [6].

In order to establish the extent of interference from other elements present on the determination of sexivalent uranium by means of chlorphosphonazo I, the amount of a particular element which would lead to an error of 5% in the determination of uranium was determined. For this purpose, 1.5×10^{-6} mole of uranyl nitrate (3.57 ml of a solution containing 0.100 mg uranium/ml) was introduced into each of five 100-ml standard flasks; to the first four flasks were then added various amounts of a solution of the element whose interference it was required to study, and the volume of the liquid in each flask was made up to 85-90 ml. Next, 2-ml lots of an acetate buffer with pH 5.5 were added and 3.0-ml lots of 0.001 M chlorphosphonazo solution; the volumes of the solutions in each flask were made up to the mark with water and the optical density measured on a SF-4 spectrophotometer at 605 mm in a cuvette with a layer thickness of 1 cm. The value of the optical density of the solution free from the interfering element was taken as 100%. A curve of optical density (%) against content of interfering element was then constructed. From this curve the amount of interfering element which would increase or decrease the optical density by 5% was determined (Table 1).

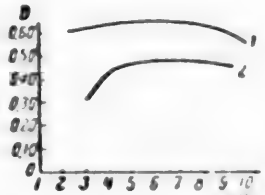


Fig. 2. The relation between light absorption of solutions of chlorphosphonazo I and of its compound with sexivalent uranium and pH (SF-4 spectrophotometer, cuvette with layer thickness 1 cm; optical density was measured relative to water). 1) 2×10^{-5} solution of chlorphosphonazo I at $\lambda_{max} = 515$ mμ; 2) solution of the compound at $\lambda_{max} = 605$ mμ (chlorphosphonazo I concentration 2×10^{-5} M; concentration of $UO_2(NO_3)_2$ 3×10^{-5} M.

The alkali and alkaline earth elements, as well as ions such as chloride, nitrate, sulfate, perchlorate, and acetate, do not interfere with uranium determination.

As the results in Table 1 show, there is no essential difference in the interference from metal cations on the results of uranium determination whether chlorphosphonazo I or arsenazo are used. Anions under the same conditions interfere to a considerably lesser extent. In this connection masking of interfering elements during determination of uranium with chlorphosphonazo I is more effective than is the case when arsenazo is used.

Since interference from a number of elements is fairly high during determination of uranium in solutions which have a complex composition, it is necessary to carry out a preliminary separation of uranium by extraction with tributyl phosphate or other extractants.

Method. To 1-5 ml of test solution is added 25 ml of a 60% ammonium nitrate solution containing 0.25% sodium ethylenediaminetetracetate (EDTA-Na); dilute ammonia solution (1:1) is next added until the pH is 2.5-3.0 (until the violet color of methanyl yellow changes to a rosy yellow) and the uranium extracted with 15 ml of a 20% solution of tributyl phosphate in carbon tetrachloride; the organic phase is filtered through a dry filter into another funnel. The aqueous layer is extracted once again with 10 ml of the 20% solution of tributyl phosphate in carbon tetrachloride. The combined extracts are washed with 25 ml of 60% ammonium nitrate solution, and after removal of the aqueous phase, the uranium is reextracted from the organic phase with 15 ml of a 0.005% solution of chlorphosphonazo I in a buffer mixture with pH 5.2 (25 g of sodium acetate and 5 ml of glacial acetic acid in 1 liter of solu-

TABLE 1. The Interfering Effect of Elements on the Photometric Determination of Uranium with Chlorphosphonazo and Arsenazo

Interfering elements of ions	The form in which the element or ion was taken	Proportion by weight of interfering element or ion to amount of uranium, which leads to an error of 5% in uranium determination	
		chlorphosphonazo	arsenazo
Al	$Al(NO_3)_3 \cdot 9H_2O$	1 : 70(+)*	1 : 70(+)
Be	$Be(NO_3)_2 \cdot 3H_2O$	1 : 70(+)	1 : 70(+)
Sn^{IV}	$SnCl_4$	1 : 35(−)	1 : 30(−)
Zr	$Zr(NO_3)_4 \cdot 5H_2O$	1 : 20(+)	1 : 25(+)
Cu	$Cu(NO_3)_2 \cdot 3H_2O$	1 : 20(−)	—
Fe^{III}	$Fe(NO_3)_3 \cdot 9H_2O$	1 : 15(+)	1 : 15(+)
Th	$Th(NO_3)_4 \cdot 4H_2O$	1 : 12(+)	1 : 15(+)
Bi	$Bi(NO_3)_3 \cdot 5H_2O$	1 : 12(−)	—
Tc^{III}	$Tl(NO_3)_3$	1 : 12(−)	—
Tc^{I}	Tl_2SO_4	1 : 7,5(−)	—
Ce^{IV}	$Ce(OH)(NO_3)_3 \cdot 3H_2O$	1 : 5(+)	—
Rare earths	Nitrates	1 : 3,5(+)	—
Hg^{II}	$Hg(NO_3)_2 \cdot 0,5\ H_2O$	1 : 3,5(−)	—
V^{IV}	$(VO)SO_4$	1 : 3,5(−)	—
Co	$Co(NO_3)_2$	2 : 1(−)	—
Mn^{II}	$Mn(NO_3)_2$	3,0 : 1(+)	—
Cr^{III}	$Cr(NO_3)_3 \cdot 9H_2O$	3,0 : 1(+)	—
Ni	$Ni(NO_3)_2$	10 : 1(−)	—
Cd	$Cd(NO_3)_2$	30 : 1(+)	—
Zn	$Zn(NO_3)_2$	70 : 1(−)	—
$C_6H_5O_7^{3-}$	Ammonium citrate	3,5 : 1(−)	1 : 1
$C_4H_4O_6^{2-}$	Potassium tartrate	15 : 1(−)	4 : 1
$C_2O_4^{2-}$	Potassium oxalate	1 : 1(−)	1 : 4
EDTA-Na		6 : 1(−)	2 : 1
F^-	NH_4F	2 : 1(−)	1 : 4
VO_3^-	NH_4VO_3	10 : 1(−)	2 : 1
PO_4^{3-}	Na_2HPO_4	15 : 1(−)	3 : 1
$Cr_2O_7^{2-}$	$K_2Cr_2O_7$	70 : 1(−)	10 : 1

*The + sign denotes a positive error, while − denotes a negative error.

TABLE 2. Photometric Determination of Sexivalent Uranium with Chlorphosphonazo

U^{VI} taken, μg	Optical density of the aqueous phase	U^{VI} found, μg	Error, %	U^{VI} taken, μg	Optical density of the aqueous phase	U^{VI} found, μg	Error, %
5	0,034	5,00	0	75	0,507	74,55	−0,6
10	0,069	10,15	+1,5	100	0,685	100,7	+0,7
15	0,103	15,15	+1,0	125	0,845	124,2	−0,6
30	0,203	29,85	−0,5	150	1,010	148,5	−1,0
50	0,337	49,55	−0,9				

tion). After removal of the organic phase, the optical density of the colored aqueous phase is measured on an SF-4 spectrophotometer at 605 mμ in a cuvette with a layer thickness of 1 cm, relative to a 0.005% chlorphosphonazo solution. The uranium content is found by means of a calibration curve (Fig. 4); the calibration curve is constructed on

the basis of a standard solution of uranyl nitrate containing 25 μg uranium/ml. The experimental error does not exceed ±1.5% (Table 2).

Zirconium, thorium, iron, beryllium, and aluminum present in the original test solution in amounts respectively 150, 450, 500, 1500, and 5000 times greater than the amount of uranium do not interfere with the determination. Interference from other elements is considerably less.

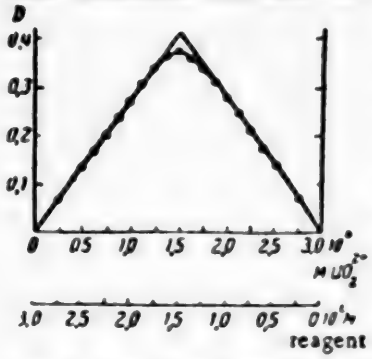


Fig. 3. Molar ratios during interaction of chlorphosphonazo I with UO_2^{2+}.

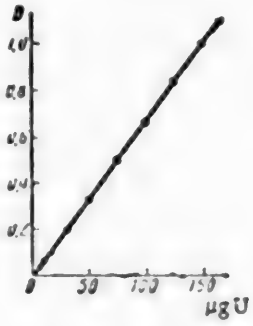


Fig. 4. Calibration curve for the determination of sexivalent uranium with chlorphosphonazo I (spectrophotometer SF-4, cuvette with layer thickness 1 cm, wave length 605 mμ; the optical density was measured with respect to a 0.005% chlorphosphonazo I solution).

Synthesis of Chlorphosphonazo.* To 2.07 g (0.01 mole) of 5-chloro-2-aminobenzenephosphonic acid (for preparation of this compound see [10]) are added 30 ml of water and 2 ml of concentrated hydrochloric acid; a solution of 0.85 g sodium nitrite in 5 ml of water is added dropwise at 0-7°. The solution of 5-chloro-2-diazobenzenephosphonic acid obtained is added to 3.0 g (0.1 mole) of chromotropic acid dissolved in 75 ml of 10% sodium acetate solution. After the reaction mixture has been stirred for 10-15 min it is acidified with hydrochloric acid (sp.gr. 1.18) until an acid reaction to Congo red is obtained. The product which separates out is filtered off and then redissolved on heating in 50 ml of water; after this solution has cooled the material is reprecipitated by addition of 25 ml of hydrochloric acid. The precipitate is filtered off, washed with 5% hydrochloric acid solution, and dried at 90-100°; the yield is 2.6 g. When the product is heated further to constant weight at 160°, it loses 8.78% by weight; this corresponds to three molecules of water of crystallization

Found %: P 5.62; S 11.48; N 5.09; Na 4.05

$C_{13}H_{11}O_{11}N_2S_2PClNa$. Calculated %: P 5.35; S 11.41; N 4.99; Na 4.11

SUMMARY

It has been shown that 2-(4-chloro-2-phosphonobenzeneazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid (called chlorphosphonazo I for short) is suitable for the photometric determination of sexivalent uranium, and possesses properties similar to those of 2-(2-arsenobenzeneazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid (arsenazo). The main difference between chlorphosphonazo I and arsenazo is that the compound which chlorphosphonazo I forms with sexivalent uranium is more stable than the corresponding compound formed between uranium and arsenazo, so that uranium can be determined in solutions with higher acidity when chlorphosphonazo I is used. When sexivalent uranium is determined by means of chlorphosphonazo I, interference from masking agents is also considerably less.

A photometric method for the determination of sexivalent uranium with chlorphosphonazo I is suggested, in which uranium is separated beforehand from interfering elements by extraction.

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ISOLATION OF URANIUM AS AMMONIUM URANYL PHOSPHATE AND ITS GRAVIMETRIC DETERMINATION BY CALCINATION TO $U_2O_3P_2O_7$

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Of the series of sparingly soluble compounds formed during the interaction of uranyl ions with phosphoric acid, ammonium uranyl phosphate $NH_4UO_2PO_4 \cdot 3H_2O$ is the most valuable in analytical practice. Unfortunately, the solubility product of this compound ($4.36 \cdot 10^{-27}$ at 19-20°) has only been determined by dissolving the solid phase in solutions of nitric and sulfuric acids [1]. Published results on the possibility of a gravimetric determination of uranium by calcination of this compound to uranyl pyrophosphate are contradictory [2,3], and the calcination process itself requires some special precautions [2]. We decided therefore to determine the solubility product of $NH_4UO_2PO_4 \cdot 3H_2O$, and to establish the possibility of determining uranium gravimetrically by calcining this compound to $U_2O_3P_2O_7$.

The ammonium uranyl phosphate used for the present studies was prepared as follows: 100 g of uranyl nitrate $UO_2(NO_3)_2 \cdot 6H_2O$ and 40 g of ammonium nitrate were dissolved in 500 ml of 2 N nitric acid. The solution obtained was heated to 80° and 26 g of diammonium hydrogen phosphate, dissolved in a small volume of water, added. A bright-yellow precipitate immediately appeared. After cooling to room temperature, the precipitate was filtered off and washed six times with distilled water. Uranium was determined in the air-dried product by the hydrosulfite-phosphate method [4]; ammonium was determined acidimetrically after distilling it off as ammonia; phosphorus was determined colorimetrically with vanadate-molybdate [5], and water by Karl Fischer reagent. The salt obtained was found to contain 62.16% UO_2^{2+}, 3.93% NH_4^+, 21.36% PO_4^{3-}, and 12.46% H_2O, i.e., it has the composition $NH_4UO_2PO_4 \cdot 3H_2O$.

A thermogravigram obtained by E. P. Chernyavenkova for this salt is shown in the figure. Interpretation of the pyrolysis curve shows that the following processes occur on heating:

Conversion temperature, range, °C	Process	Loss in wt., %	
		found	calculated
20—120	$NH_4UO_2PO_4 \cdot 3H_2O \rightarrow NH_4UO_2PO_4 + 3H_2O\uparrow$	12.42—12.46	12.36
275—350	$NH_4UO_2PO_4 \rightarrow UO_2HPO_4 + NH_3\uparrow$	4.49— 4.85	4.45
500—700	$2UO_2HPO_4 \rightarrow (UO_2)_2P_2O_7 + H_2O\uparrow$	2.55— 2.52	2.32
700—1100	$2(UO_2)_2P_2O_7 \rightarrow 2(U_2O_3)P_2O_7 + O_2\uparrow$	2.30— 2.19	2.24

In order to confirm the correctness of the results obtained during pyrolysis of ammonium uranyl phosphate, and to choose the gravimetric form in which uranium is to be determined, the following experiments were carried out:

a) on drying $NH_4UO_2PO_4 \cdot 3H_2O$ in a vacuum desiccator the salt gradually gives up its water of crystallization;

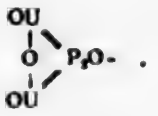
b) at 120-220° anhydrous ammonium uranyl phosphate is obtained, which absorbs water from the atmosphere;

c) on calcining the preparation at 400°, uranyl hydrophosphate UO_2HPO_4 is obtained, which is also hygroscopic;

d) uranyl pyrophosphate $(UO_2)_2P_2O_7$ exists over a narrow temperature range; accordingly, it is only by strict control of temperature and calcining time that it is possible to get a compound with the composition indicated above;

e) the compound with composition $U_2O_3P_2O_7$ is readily obtained by calcining ammonium uranyl phosphate, uranyl hydrophosphate, and uranyl pyrophosphate at 900°. On increasing the temperature further its composition does not change (checked up to 1200°). The compound $U_2O_3P_2O_7$ has a yellow-green color; it is not hydroscopic, contains 68.21% uranium, and appears to be homogeneous according to X-ray structural studies.

On dissolving an aliquot of the compound $U_2O_3P_2O_7$ in 85% phosphoric acid on heating, a solution with a green color is obtained. By oxidimetric titration it was established that the compound contains 33.9% of the uranium in a quadrivalent state (mean of six determinations), i.e., half of the uranium present. In our opinion this compound is a pyrophosphate of quinquevalent uranium



which on dissolving in phosphoric acid dissociates into UO_2^{2+} and U^{IV}. The composition $(UO_2)_2P_2O_7 \cdot (UO)_2P_2O_7$ with the same gross formula is less probable.

Thermogravimetric curve of ammonium uranyl phosphate.

Three series of experiments were carried out to determine the solubility product of $NH_4UO_2PO_4 \cdot 3H_2O$. In the first of these series (points 1-8) 1-g portions of $NH_4UO_2PO_4 \cdot 3H_2O$ at 25 ± 0.2° in 100-ml standard flasks, varying amounts of 0.1 N hydrochloric acid were added, and the volumes made up to the mark with water. In the second series of experiments (points 9-15), 10 ml of 0.1 M diammonium hydrogen phosphate solution was added in addition to each of the flasks. In the third series (point 16-20) the solid phase was obtained by pouring together solutions of uranyl nitrate and diammonium hydrogen phosphate. The flasks and their contents were shaken and the temperature thermostatted automatically until equilibrium was reached (72 hr). When equilibrium had been reached the solutions were filtered through a glass filter with a No. 4 porous disc. The uranium, phosphorus, and ammonium contents of the filtrates were determined as indicated above, while the pH was measured with a quinhydrone electrode using a PPTV-1 potentiometer. The results of some of the experiments (odd numbers) are given in Table 1.

TABLE 1. Experimental Results and Results of Calculations of the Solubility Product of $NH_4UO_2PO_4 \cdot 3H_2O$ at 25 ± 02°

Expt. No.	Equilibrium concentrations, moles/liter				Solubility product $P \cdot 10^{-28}$
	uranium (C_1)	phosphate (C_2)	ammonium (C_3)	$[H^+]$	
1	$3,0 \cdot 10^{-4}$	$1,53 \cdot 10^{-4}$	$2,8 \cdot 10^{-3}$	$7,943 \cdot 10^{-3}$	3,28
3	$3,30 \cdot 10^{-3}$	$3,32 \cdot 10^{-4}$	$5,90 \cdot 10^{-3}$	$7,08 \cdot 10^{-3}$	3,69
5	$7,20 \cdot 10^{-3}$	$7,23 \cdot 10^{-4}$	$7,79 \cdot 10^{-3}$	$1,349 \cdot 10^{-2}$	3,51
7	$1,15 \cdot 10^{-2}$	$1,13 \cdot 10^{-3}$	$1,13 \cdot 10^{-2}$	$1,950 \cdot 10^{-2}$	4,29
9	$2,80 \cdot 10^{-4}$	$1,00 \cdot 10^{-3}$	$2,04 \cdot 10^{-2}$	$6,31 \cdot 10^{-3}$	4,56
11	$1,475 \cdot 10^{-3}$	$1,16 \cdot 10^{-3}$	$2,19 \cdot 10^{-2}$	$1,443 \cdot 10^{-2}$	2,83
13	$4,025 \cdot 10^{-3}$	$1,14 \cdot 10^{-3}$	$2,48 \cdot 10^{-2}$	$2,042 \cdot 10^{-2}$	2,88
15	$1,18 \cdot 10^{-2}$	$2,19 \cdot 10^{-3}$	$3,08 \cdot 10^{-2}$	$3,236 \cdot 10^{-2}$	5,14
17	$2,80 \cdot 10^{-3}$	$2,38 \cdot 10^{-3}$	$3,01 \cdot 10^{-2}$	$1,097 \cdot 10^{-2}$	3,45
19	$9,20 \cdot 10^{-3}$	$8,95 \cdot 10^{-3}$	$3,62 \cdot 10^{-2}$	$2,344 \cdot 10^{-2}$	5,02

In calculating the solubility product of ammonium uranyl phosphate, the following must be taken into account:

a) the hydrolysis of the uranyl ion ($K_h = 6.4 \cdot 10^{-5}$ [6]; its equilibrium concentration is calculated by means of the equation

$$[UO_2^{2+}] = \frac{C_1[H^+]}{K_h[H^+]}; \quad (1)$$

b) dissociation of phosphoric acid through all its three stages ($K_1 = 7.51 \cdot 10^{-3}$, $K_2 = 6.23 \cdot 10^{-8}$, $K_3 = 4.8 \cdot 10^{-13}$); the equilibrium concentration of $[PO_4^{3-}]$ is calculated by means of the equation

$$[PO_4^{3-}] = \frac{C_2 \cdot K_1 \cdot K_2 \cdot K_3}{[H^+]^3 + K_1[H^+]^2 + K_1K_2[H^+] + K_1K_2K_3}. \quad (2)$$

Hydrolysis of NH_4^+ over the pH range examined can be ignored.

Results of calculations of the solubility products by means of the equation

$$P = [NH_4^+][UO_2^{2+}][PO_4^{3-}] = \frac{C_1 \cdot C_2 \cdot C_3 \cdot K_1 \cdot K_2 \cdot K_3 \cdot [H^+]}{(K_r + [H^+])([H^+]^3 + K_1[H^+]^2 + K_1K_2[H^+] + K_1K_2K_3)} \quad (3)$$

are given in Table 1.

The mean value of the solubility product obtained as the result of a statistical treatment of 20 experiments proved to be equal to $P = (3.6 \pm 0.4) \cdot 10^{-24}$ at a confidence level of 0.95. The solubility of ammonium uranyl phosphate as a function of the pH of the solution, the concentrations of the phosphate ions ($C_2 = 1 \cdot 10^{-2}$ M) and ammonium salts ($C_3 = 1$ M) being constant, was calculated by means of equation (3). The solubility is characterized by the following results:

pH	2.0	3.0	4.0	5.0	7.0
C_1, M	$2 \cdot 10^{-6}$	$2 \cdot 10^{-10}$	$3 \cdot 10^{-12}$	$1 \cdot 10^{-13}$	$2 \cdot 10^{-13}$

It follows from these results that quantitative precipitation of uranium as ammonium uranyl phosphate, under the conditions indicated, is possible in solutions having a pH greater than 3. Specially conducted experiments confirmed this assumption.

In weakly acid solutions (pH 3.0-5.0) the sparingly soluble phosphates of a number of other metal ions will be precipitated together with ammonium uranyl phosphate, but by introducing ethylenediaminetetraacetic acid (H_4Y) it is possible to increase the selectivity of uranium separation significantly.

To determine the permissible concentration of interfering metallo-ion Me^{n+} (C_4, M) at which this ion will not be precipitated in the form of its phosphate at known pH values, concentrations of H_4Y (C_5, M), and phosphate concentration (C_2, M), the following processes must be taken into account:

$$Me^{n+} + H_2O = Me(OH)^{(n-1)+} + H^+, \quad K_h = \ldots \quad (4)$$

$$H_3PO_4 = H_2PO_4^- + H^+, \quad K_1 = 7.5 \cdot 10^{-3} \quad (5)$$

$$H_2PO_4^- = HPO_4^{2-} + H^+, \quad K_2 = 6.3 \cdot 10^{-8} \quad (6)$$

$$HPO_4^{2-} = PO_4^{3-} + H^+, \quad K_3 = 3.6 \cdot 10^{-13} \quad (7)$$

$$3Me^{n+} + nPO_4^{3-} = (Me_3)(PO_4)_n \quad P = \ldots \quad (8)$$

In the pH range we are interested in, ethylenediaminetetraacetic acid will exist in the form of the ion H_2Y^{2-}; accordingly, the following processes must be taken into account:

$$H_4Y \rightleftarrows HY^{3-} + H^+, \qquad K_6 = 6{,}92 \cdot 10^{-7}\ [7] \tag{9}$$

$$HY^{3-} \rightleftarrows Y^{4-} + H^+, \qquad K_5 = 5{,}47 \cdot 10^{-11}\ [7] \tag{10}$$

$$Me^{n+} + Y^{4-} \rightleftarrows MeY^{(4-n)-}, \qquad 1/K_4 = \ldots \tag{11}$$

We denote the equilibrium concentrations as follows $[Me^{n+}] = x$, $[Me(OH)^{(n-1)+}] = y$, $[H^+] = h$, $[H_3PO_4] = V$, $[H_2PO_4^-] = W$, $[HPO_4^{2-}] = Z$, $[PO_4^{3-}] = U$, $[H_3Y^{3-}] = l$, $[HY^{3-}] = a$, $[Y^{4-}] = b$, and $[MeY^{(4-n)-}] = t$, M.

Applying the law of mass action to processes (4-11) and taking into account conversion of the original materials, we have:

$$K_1 x = yh \tag{12}$$

$$K_2 V = Wh \tag{13}$$

$$K_3 W = Zh \tag{14}$$

$$K_4 Z = Uh \tag{15}$$

$$x^3 U^4 < P \tag{16}$$

$$K_6 l = ah \tag{17}$$

$$K_5 a = bh \tag{18}$$

$$xb = K_4 t \tag{19}$$

$$C_0 = x + y + t \tag{20}$$

$$C_0 = l + a + b + t \tag{21}$$

$$C_3 = V + W + Z + U \tag{22}$$

To calculate C_4 from equations (17), (18), (19), and (21) we find t:

$$t = \frac{K_4 K_5 C_0 x}{K_4 K_5 x + (h^3 + K_6 h + K_6 K_5) K_4}. \tag{23}$$

Substituting t from (23) in (20) and taking into account (12) and (16), we obtain:

$$C_4 < \frac{P^{1/3}}{U^{4/3}} \left[1 + \frac{K_1}{h} + \frac{K_4 K_5 C_0 x}{K_4 K_5 \dfrac{P^{1/3}}{U^{4/3}} + (h^3 + K_6 h + K_6 K_5) K_4} \right], \tag{24}$$

where U is calculated from (13), (14), (15), and (22) by means of the equation

$$U = \frac{C_3 K_1 K_2 K_3}{h^3 + K_1 h^2 + K_1 K_2 h + K_1 K_2 K_3}. \tag{25}$$

The inequality (24) enables one to evaluate the permissible concentration of interfering metallo-ion (C_4, M) at which it will not be precipitated as its phosphate, as a function of the concentration of hydrogen ions, excess precipitant, and original H_4Y concentration.

Results of calculations based on equation (24) are given in Table 2.

TABLE 2. Permissible Concentrations of Interfering Metallo-Ions at Which Selective Precipitation of $NH_4UO_2PO_4 \cdot 3H_2O$ Will Occur When $C_0 = 3{,}4 \cdot 10^{-2}$M, $C_3 = 1 \cdot 10^{-2}$M, as a Function of the pH of the Solution

Sparingly soluble compounds	Solubility product	Instability constant K_4 [8]	Permissible impurity concentration		Hydrolysis constant of the metallo-ion
			pH 3,0	pH 5,0	
$Ca_3(PO_4)_2$	$2{,}0 \cdot 10^{-29}$	$1{,}58 \cdot 10^{-11}$	7,9	$5{,}0 \cdot 10^{-3}$	$2{,}5 \cdot 10^{-13}$
$Mg_3(PO_4)_2$	$2{,}5 \cdot 10^{-13}$	$2{,}04 \cdot 10^{-9}$	$1{,}8 \cdot 10^{+6}$	$(3{,}7 \cdot 10^{+3})$	$2{,}0 \cdot 10^{-10}$
$Pb_3(PO_4)_2$	$7{,}9 \cdot 10^{-43}$	$9{,}12 \cdot 10^{-19}$	$3{,}4 \cdot 10^{-3}$	$3{,}4 \cdot 10^{-3}$	$3{,}3 \cdot 10^{-7}$
$Zn_3(PO_4)_2$	$9{,}1 \cdot 10^{-33}$	$3{,}16 \cdot 10^{-17}$	$6{,}5 \cdot 10^{-1}$	$3{,}5 \cdot 10^{-3}$	$2{,}5 \cdot 10^{-16}$
$AlPO_4$	$5{,}8 \cdot 10^{-19}$	$7{,}41 \cdot 10^{-17}$	$3{,}7 \cdot 10^{-3}$	$3{,}1 \cdot 10^{-3}$	$1{,}25 \cdot 10^{-6}$
$FePO_4$	$1{,}3 \cdot 10^{-22}$	$7{,}94 \cdot 10^{-18}$	$3{,}4 \cdot 10^{-3}$	$3{,}2 \cdot 10^{-3}$	$3{,}3 \cdot 10^{-9}$

The results given in Table 4 show that the method is applicable to the determination of uranium in its technical salts, oxides, concentrates, and alloys. Determinations can be carried out with reasonable accuracy and reliability. their complete masking and ensure selective precipitation of uranium as ammonium uranyl phosphate.

On the basis of what has been said above, and on a whole series of preliminary experiments, the following technique is suggested for the preparation of a readily filterable precipitate of ammonium uranyl phosphate, and for subsequent gravimetric determination of uranium. An aliquot of test material is taken such that its uranium content is about 200-300 mg. Dissolution of aliquots of sodium uranyl acetate, uranium tetrafluoride, uranoso uranic oxide, uranium concentrates, uranium ores and alloys is carried out in nitric and hydrochloric acids, with subsequent evaporation of the solutions to 2-3 ml. In the case of alloys of uranium with zirconium, 10 ml of a 0.1% ammonium fluoride solution is added beforehand; decomposition is carried out as indicated above and then 10 ml of 30% tartaric acid solution added. The solutions obtained are diluted with water to 10-15 ml, heated to the boil, and filtered when necessary. The precipitate on the filter and the beaker are washed with a hot solution which is 5.5% with respect to ammonium chloride and 1% with respect to hydrochloric acid; 80-90 ml of this solution is used for washing. To the solutions obtained is added 10 ml of 10% NH_4ethylenediaminetetracetate solution. When test materials contain a large amount of aluminum, the amount of NH_4ethylenediaminetetracetate added is equivalent to the stoichiometric amount necessary for complexing all the aluminum plus 5-10 ml in excess. The solution is next heated to the boil and 0.2 M diammonium hydrogen phosphate added until a precipitate appears. The liquid is boiled for one minute and an additional amount of ammonium phosphate solution added until the total volume is 10 ml. After 5 min, 0.6-0.8 ml of a 0.1% aqueous solution of alizarin red is added; this is followed by ammonia solution (1-3) until a rose color appears (pH 3.7-5.2). After 5-10 min the solution is decanted onto a white band filter paper; the precipitate is transferred onto the filter paper and washed with hot 2% ammonium chloride solution containing 0.1% ammonium ethylenediaminetetracetate. 80-170 ml of wash liquor is used for each precipitate. The precipitates are placed in tared crucibles; the filter papers are ashed, and the whole calcined at 900-1000° for one hour; the residue is finally weighed as $U_2O_2P_2O_7$. A blank is carried out in parallel, and the weight of the filter paper ash subtracted from the weight obtained. Results of a check on the method using synthetic mixtures are given in Table 3. A standard solution of uranyl nitrate and aqueous solutions of the salts of the corresponding elements were used for these experiments.

TABLE 3. Results of Statistical Treatment of Experimental Results on Determination of Uranium in Solutions Containing Impurities

Added				No. of uranium determinations	Uranium found, mg	Mean square error	
uranium, mg	impurity, mg	H_4Y, g	tartaric acid, g			mg	% (relative)
286.6	—	1.0	—	12	286.6	±0.30	±0.10
286.6	$20Fe^{3+}$, $20Al^{3+}$, $20V^{5+}$, $20Na^{+}$	2.5	—	12	286.9	±0.58	±0.20
241.7	35 Cr^{3+}	1.5	—	10	241.7	±0.12	±0.05
241.7	35 Zr^{4+}	1.0	3.0	11	241.9	±0.15	±0.06
241.9	240 Al^{3+}	4.5	—	11	241.9	±0.13	±0.06

The results given in Table 3 show that the method gives correct and readily reproducible results for uranium determination. The loss of uranium with the filtrates, as determined by luminescent analysis, does not exceed 0.1 mg. It should be pointed out that in the presence of chromium, during adjustment of the requisite pH, the indicator changes its color from yellow to red-violet, while in the presence of tartaric acid it changes from yellow to orange.

Determination of uranium in actual test materials (Table 4) is carried out as indicated in the procedure outlined above.

The results given in Table 4 show that the method is applicable to the determination of uranium in its technical salts, oxides, concentrates, and alloys. Determinations can be carried out with reasonable accuracy and reliability.

One analyst can carry out 10-12 uranium determinations in six hours.

TABLE 4. Results of a Check on the Method

Test material	Uranium content, %	Suggested method			
		no. of determinations	uranium found, %	mean square error	
				% (absolute)	% (relative)
Sodium uranyl acetate	50,76	11	50,80	±0,13	±0,25
Uranoso uranic oxide	82,91	11	82,99	±0,16	±0,19
Uranium tetrafluoride	72,51	11	72,77	±0,16	±0,22
Concentrate	51,60	11	51,59	±0,16	±0,31
Ore	15,26	12	15,40	±0,10	±0,60
Alloy with Zr	89,61	12	89,80	±0,11	±0,13
Alloy with Al	70,15	11	70,24	±0,14	±0,20

SUMMARY

The solubility product of ammonium uranyl phosphate $NH_4UO_2PO_4 \cdot 3H_2O$ has been determined. It was found to be equal to $(3.6 \pm 0.4) \cdot 10^{-26}$ at 25°.

A gravimetric method has been developed for the determination of uranium; it is based on precipitation of ammonium uranyl phosphate in the presence of ammonium ethylenediaminetetracetate, and weighing the uranium as $U_3O_8P_2O_7$.

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THE USE OF C_7-C_9 FATTY ACID FRACTION FOR SEPARATION OF IRON AND COPPER FROM COBALT

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Photometric determination of small amounts of cobalt by means of nitroso-R-salt in materials containing large amounts of iron, copper, nickel, and chromium is a problem which has hitherto proved difficult and has attracted the attention of rearch workers. Determination of about 0.6% cobalt can be carried out by this method without separating it from the other elements in the presence of up to 70% iron, 5% nickel, and 15% copper [1,2]. During cobalt determination some authors have masked iron with sodium fluoride or phosphoric acid [3]. In order to increase the accuracy of determination of small amounts of cobalt in steels and iron, iron has been separated by extraction with isopropyl ether or in the form of its complex with cupferron [4,5]. Dipyridylmethane has been used for separating cobalt from nickel, manganese, chromium, zinc, cadmium, magnesium, barium, and calcium [6]. Copper can be separated from cobalt by means of lead diethyldithiocarbamate [7,8]. For the analysis of ores containing large amounts of iron and copper, copper has been separated with potassium nitrite. A colorimetric finish with nitroso-R-salt is used. The method is very tedious and takes a long time. Despite this, the method is widely used at present [9]. Gindin et al.[10] have for technological purposes, suggested separation of iron and copper from cobalt by means of a mixture of saturated acids with carbon numbers 7 to 9. Kuznetsov has shown that the extractability of copper salts of fatty acids increases with increasing hydrocarbon chain length [11]. Extraction of copper salts of fatty acids for the quantitative determination of copper has been described [12].

The present article is devoted to a description of a method for the photometric determination of cobalt by means of nitroso-R-salt after separation of cobalt from iron by means of fatty acids, and from copper by means of lead diethyldithiocarbamate. Dipyridylmethane is used for separating cobalt from nickel and a number of other elements.

Extraction of Iron and Copper with a Fatty Acid Mixture. A 20% solution of a mixture of C_7-C_9 fatty acids in chloroform was used for extraction.

The iron alum and cupric sulfate solutions used contained about 0.004 g Fe per ml and about 0.004 g Cu per ml respectively. Buffer mixtures were prepared by mixing 0.2 N solutions of acetic acid and sodium acetate.

The fatty acid mixture is produced by the Combine of Synthetic Fatty Acids and Higher Alcohols, Shebekino, according to GOST 8622-57.

Five ml of the iron or copper salt solution, 50 ml of buffer mixture, and 55 ml of the fatty acid solution were introduced into a 200-ml separating funnel. Extraction was carried out for 2 min. After the layer had separated, the organic layer was poured into another separating funnel and copper and iron extracted into the aqueous phase, extraction being carried out twice with 20-ml lots of hydrochloric acid (1 : 4) for one minute. Iron was determined in the acid extract iodometrically after its precipitation with ammonia and subsequent dissolution of the hydroxide; copper was precipitated with thiosulfate after evaporation of the acid extract with sulfuric acid until all the chlorides had been removed; the determination was finished iodometrically.

Results of experiments on extraction of copper and iron are given in Table 1.

The results given in Table 1 show that extraction of iron and copper from acetic acid solutions is almost complete at pH values close to those for the precipitation of the hydroxides of these metals; this is in agreement with published results [10].

Palmitic acid (m.p. 64°) was also tested as an extractant. Four g of powdered palmitic acid was scattered into a beaker containing the iron or copper salt solution; the mixture was then heated to the boil and boiled for 2 min. After cooling, the solution and the reextract obtained by boiling the solidified palmitic acid with hydrochloric acid were analyzed.

TABLE 1. Relation between Extraction of Iron and Copper with Fatty Acids and the pH of the Aqueous Solution (22.2 mg iron and 20.2 mg of copper were taken in all the experiments)

pH of the aqueous solution	Iron found in the reextract, mg	Iron extracted, %	Copper found in the reextract, mg	Copper extracted, mg	Separation of iron and copper			
					found in the aqueous solution after extraction		found in the reextract	
					iron, mg	copper, mg	iron, mg	copper, mg
3,7	8,5	38,3	5,6	27,7	15,9	20,2	6,0	Trace
4,3	22,2	100	15,1	74,7	0,3	19,3	21,5	0,8
4,6	22,2	100	18,6	92,1	0,3	8,0	21,3	12,2
5,0	22,2	100	19,8	98,0	0,2	3,4	21,5	16,7
5,4	22,4	100	20,0	99,0	0,2	2,2	21,3	18,1
5,6	22,1	99,5	20,0	99,0	0,3	0,9	21,2	18,8

TABLE 2. Separation of Trivalent Iron from Cobalt in Sulfuric Acid Solutions

20 mg iron taken*		1000 mg iron taken*		1000 mg iron taken**	
Cobalt, mg					
taken	found	taken	found	taken	found
0,01	0,011	0,02	0,02	0,02	0,021
0,02	0,02	0,04	0,04	0,04	0,043
0,03	0,03	0,06	0,059	0,06	0,06
0,04	0,039	0,08	0,08	0,08	0,08
0,05	0,05	0,10	0,10	0,10	0,099
0,06	0,057				
0,07	0,078				
0,08	0,074				

* Iron alum solution (the preparation contained 0.002% cobalt).

** Ferric sulfate solution prepared from Armco iron containing 0.014% cobalt.

These experiments showed that extraction does not depend to a significant extent on the length of the hydrocarbon chain, at a fixed pH.

Separation of Cobalt from Iron, Copper, and Other Metals. It was established that cobalt is not extracted with the chloroform solution of fatty acids at pH 5.6, the optimum pH for separation of iron and copper.

Solutions of iron and copper salts, and a cobalt sulfate solution containing 0.00001 g Co per ml were introduced into a separating funnel. A 50% solution of sodium acetate was added dropwise until the pH was about 5 according to universal indicator paper. Thirty ml of buffer solution (pH 5.6) and 50-100 ml of the 20% solution of fatty acids in chloroform were added, and the whole shaken for 1-2 min; extraction was repeated until a colorless organic phase was obtained. The aqueous layer was washed free from fatty acids by shaking with pure chloroform. The aqueous layer was transferred to a 250-ml conical flask, and 20 ml of 50% sodium acetate was added; the mixture was heated to the boil and then evaporated to reduce its volume; 10 ml of 0.5% nitroso-R-salt solution was added and the liquid boiled for one minute; 25 ml of nitric acid (1 : 1) next was added and the liquid again boiled for one minute; it was finally cooled and transferred to a 200-ml standard flask.

Calibration curves were constructed using pure cobalt sulfate solutions, the extraction step being omitted.

Results of experiments on the separation of iron from cobalt are given in Table 2. The optical density was measured relative to the "blank" solutions obtained after extracting the iron. 1000 mg of iron can be separated by carrying out two extractions with 100- to 120-ml lots of the fatty acid solution.

TABLE 3. Separation of Copper from Cobalt with Lead Diethyldithiocarbamate

Copper taken, mg	Cobalt, mg		Copper taken, mg	Cobalt, mg	
	taken	found		taken	found
10	0,02	0,02	100	0,02	0,02
10	0,04	0,04	100	0,04	0,04
10	0,06	0,061	100	0,06	0,06
10	0,08	0,081	100	0,08	0,08
			1000	0,04	0,038
			1000	0,08	0,083

TABLE 4. Separation of Iron and Copper from Cobalt by means of Lead Diethyl dithiocarbamate and the Fatty Acids in Nitric Acid Solutions

20 mg copper and 20 mg iron taken		100 mg copper and 100 mg iron taken	
Cobalt, mg			
taken	found	taken	found
0,02	0,023	0,02	0,02
0,04	0,038	0,04	0,039
0,06	0,059	0,06	0,061
0,08	0,078	0,08	0,081

Experiments showed further that complete separation of 400 mg of copper is only achieved after 10-12 extractions, although the bulk of the copper is extracted during the first operation. Accordingly, we checked on the possibility of separating copper with a solution of lead diethyldithiocarbamate in chloroform (4.5 g lead per liter). To 50 ml of cupric nitrate solution prepared from electrolytic copper (free from cobalt) was added cobalt sulfate solution and 50 ml of acetate buffer mixture (pH 4.1). The experimental results are given in Table 3.

It follows from these results that lead diethyldithiocarbamate completely separates copper from cobalt. The lead which passes into the aqueous solution does not interfere with the photometric determination of cobalt with nitroso-R-salt.

Table 4 contains the results for the separation of iron and copper from cobalt. Copper was extracted at pH about 3 with a solution of lead diethyldithiocarbamate in chloroform; the pH was then adjusted to 5.6 by addition of acetate buffer mixture and the iron extracted with a solution of the fatty acid mixture in chloroform. Iron and copper salts were added in the "blank" experiments.

The method described for separating iron and copper gives considerably worse results in sulfuric acid solutions, since the lead which passes into the aqueous phase is precipitated as $PbSO_4$.

Results of experiments with sulfuric acid solutions carried out as follows proved satisfactory. Iron and the bulk of the copper were extracted with the fatty acids at pH about 5, and the residual copper was extracted with lead diethyldithiocarbamate at pH about 4. Under these conditions, the amount of lead which passes into solution is small, and in the presence of acetic acid and sodium acetate a precipitate of $PbSO_4$ is not formed. During determination of 0.02, 0.04, 0.06 and 0.08 mg Co, the amounts of cobalt found were 0.02, 0.04, 0.06 and 0.08 mg respectively.

Salts of trivalent chromium and divalent maganese are not extracted by the chloroform solution of fatty acids over the pH range 3.7-7.9.

Separation of small amounts of cobalt from large amounts of nickel by means of the fatty acids is not feasible. Accordingly, in order to separate cobalt from trivalent chromium, divalent manganese, and nickel, we made use of the extraction of cobalt in the presence of ammonium thiocyanate and diantipyrylmethane [6].

Analysis of Steels and Ores. An aliquot of the solution of test material is transferred to a 250-ml separating funnel; 50% sodium acetate is added dropwise until the pH is about 5 (a drop of solution is placed on the indicator paper through a double layer of filter paper since the solution has a red color); this is followed by 30 ml of acetate buffer mixture (pH 5.6). One hundred ml of the 20% solution of fatty acids in chloroform is added and the whole shaken vigorously. Extraction is repeated until a colorless organic layer is obtained; the aqueous layer is then washed with 10 ml of chloroform; the solution is acidified with hydrochloric acid until the pH is 3-4, and the remaining copper extracted with a solution of lead diethyldithiocarbamate in chloroform. The aqueous layer is washed with about 10 ml of chloform and is poured into a 250-ml conical flask. The solution is heated to the boil and 20 ml of 50% sodium acetate solution added; 10 ml of a 0.5% solution of nitroso-R-salt is added to the boiling solution and the whole boiled for one minute; 25 ml of nitric acid (1:1) is added and the solution boiled again for one minute; it is finally cooled and transferred to a 200-ml standard flask.

When the sample contains large amounts of nickel, chromium, and manganese, the solution left after removal

TABLE 5. Determination of Cobalt in Steel (Cobalt Found in the Sample 0.016%) Sample wt. 0.2 g; Sulfuric Acid Solution

Cobalt, mg	
Taken	Found
0.04	0.039
0.07	0.071
0.10	0.099

of the iron and copper is acidified with hydrochloric acid until the pH is 1-2 according to universal indicator paper; 10 ml of a 40% ammonium thiocyanate solution and 20 ml of a 2% solution of diantipyrylmethane in 0.5 N HCl are added and shaken for 1 min, and the Co compound extracted with 10 ml of chloroform. This operation is repeated twice. When the cobalt content is high the extract is colored blue by the cobalt complex. To the organic layer contained in a separating funnel is added 20 ml of a 0.2 N sodium acetate solution and 5 ml of 0.5% nitro-R-salt solution, and the whole shaken for one minute; the organic layer is transferred to another separating funnel, while the aqueous layer is transferred to a 200-ml standard flask. Twenty ml of 0.2 N sodium acetate and 5 ml of 0.5% nitroso-R-salt solution are added again to the organic layer. After shaking, the aqueous layer is transferred to the standard flask, while the chloroform is discarded. To the aqueous solution in the standard flask is added 10 ml of nitric acid (1 : 1), and the liquid is left for 15 min. The volume is made up to the mark with water and the optical density of the solution is measured on a FÉK-M photoelectric colorimeter fitted with a green filter.

TABLE 6. Determination of Cobalt in Ores

Co found by the method suggested, %		Co found photometrically after its isolation as cobaltinitrite
Determination I	Determination II	
0.040	0.042	0.041
0.034	0.034	0.032
0.042	0 042	0.042
0.052	0.054	0.052
0.031	0.032	0.032
0.152	0.150	0.157
0.180	0.181	0.181
0.059	0.058	0.058

The "blank" solution is prepared by adding sodium acetate, nitroso-R-salt, and nitric acid to water.

A calibration curve is constructed using cobalt sulfate solution; the extraction operation is omitted.

The method has been checked by adding known amounts of cobalt to a standard sample of No. 53-a steel, containing 12.1% Cr. The optical density was measured relative to a "blank" solution obtained from an aliquot of steel to which no cobalt was added. The experimental results are given in Table 5.

Table 6 contains the results of cobalt determination in ore products containing large amounts of copper. Samples chosen for analysis were ones to which photometric determination by means of nitroso-R-salt was inapplicable without preliminary separation of cobalt. The agreement between the results obtained justifies the technique of separating cobalt by extraction.

SUMMARY

The use of a solution of C_7-C_9 fatty acids in chloroform, and of a solution of lead diethyldithiocarbamate in chloroform, is suggested for separating small amounts of cobalt from large amounts of iron and copper. A method which has been developed has been checked on synthetic solutions, steels, and ores.

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POTENTIOMETRIC DETERMINATION OF COBALT WITH FERRICYANIDE IN A GLUTAMIC ACID MEDIUM

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Quantitative oxidation of divalent cobalt in the form of its glutamate complex by mean of potassium ferricyanide has been studied potentiometrically as a function of pH and the concentration of glutamic acid and cobalt. It was established in the course of this work that the compound of divalent cobalt with glutamic acid is stable in air at a pH of 9.8-11.4, and that it is possible to oxidize it quantitatively with potassium ferricyanide. As a result of the present investigation a method has been developed for the determination of cobalt in various materials (steel, ores). The method permits determination of 1% Co in zinc, nickel, bismuth, cadmium, copper, and molybdenum. Manganese in amounts which are five times that of cobalt does not interfere.

Potassium ferricyanide is used as an oxidizing agent for the determination of cobalt in an ammoniacal medium [1-2]. Since low results are obtained during direct titration, the normal procedure is to add a solution of the sample to a standard ammoniacal solution of ferricyanide, excess of the latter being then back-titrated with a standard cobalt salt solution. The interaction of cobalt salts with ferricyanide has been studied by many authors [3-5]; Diehl and Butler [6] have replaced ammonia by ethylenediamine, which ensures more favorable conditions for carrying out titration.

Oxygen, however, readily oxidizes the ethylenediamine complex of divalent cobalt, so that it is necessary to work in an inert atmosphere. Kopanica and Doležal [7] eliminated this drawback by using glycine.

Titration with ferricyanide is the best method for determining cobalt and is characterized by high selectivity. Ways of eliminating interference from manganese have been indicated in previous articles. It has been shown that it is possible to determine manganese together with cobalt in a medium of ethylenediamine and sulfosalicylic acid [6]. The polarographic behavior of the complex salts of cobalt with glutamic acid has been studied in detail [8], as well as the oxidation of this stable compound with ferricyanide. In the present article the possibility is demonstrated of determining cobalt potentiometrically in air with potassium ferricyanide in the presence of glutamic acid. The method has given very good results during analysis of various steels and ores and is suitable as a simple method and for industrial control. Glutamic acid is readily available and is not an expensive reagent.

METHOD

Reagents: A 0.1 N solution of potassium ferricyanide was prepared from a Czech product (LAKhEMA) and was checked iodometrically. More dilute solutions were prepared by diluting the 0.1 M solution.

A standard cobalt sulfate solution was prepared from the pure product ($CoSO_4 \cdot 7H_2O$, Merck); Co concentration was established electrolytically.

The glutamic acid used was a Czech product (VITANA). The dissociation constants of glutamic acid which are given in the literature ($pK_1 = 2.19$, $pK_2 = 4.25$, $pK_3 = 9.66$ and $pK_1 = 2.16$; $pK_2 = 4.32$, $pK_3 = 9.96$), were checked by potentiometric titration with sodium hydroxide using a glass indicator electrode. The results obtained for pK_2 and pK_3 are in almost complete agreement with published results [9-13] (the pK values found were 2.3, 4.30, and 9.60). The value of pK_1 cannot be determined accurately from the titration curve (Fig. 1).

The samples of steel used conformed to international standards.

Potentiometric titration with ferricyanide was carried out on a "KRATO" instrument (Kratovkhvil Engineering School, Prague). A "Multoscope" apparatus (Laboratory Apparatus, Prague) was used for measuring the pH.

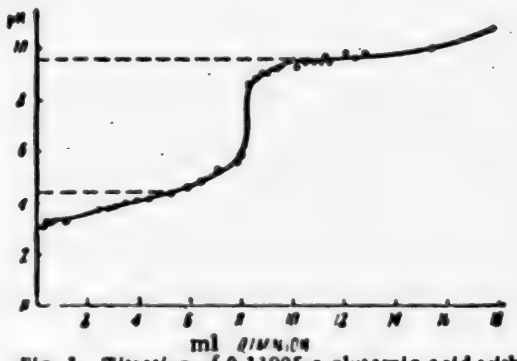

Fig. 1. Titration of 0.11205 g glutamic acid with 0.1 M NaOH (φ = 0.9747).

RESULTS

Data on the complexes of glutamic acid with metal ions have been published by many authors; these include complexes with Co^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+} [14-16], and with Cu^{2+} in an alkaline medium (polarographically [17-18] and potentiometrically [19]). The complexes of Co^{2+}, Ni^{2+}, Fe^{2+}, Mn^{2+} [20,21], as well as those of Ag^{+} [22,23] and the rare earths [24] have also been studied polarographically and by oscillographic polarography.

Glutamic acid interacts with Co^{2+} in the proportion of 2:1 [15,16,25].

The compound of cobalt with glutamic acid does not change in air, but it is oxidized by potassium ferricyanide.

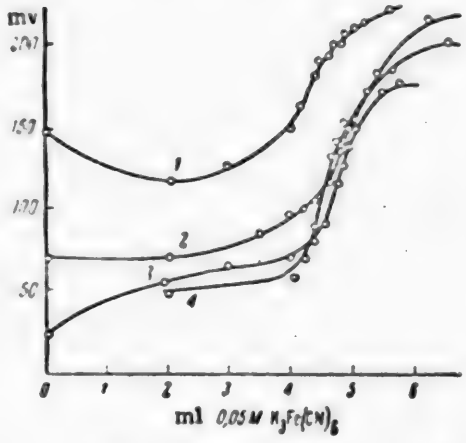

Fig. 2. Effect of pH on the oxidation of the divalent cobalt complex of glutamic acid with ferricyanide. 5 ml of 0.05 M $CoSO_4$ in 50 ml of 0.2 M glutamic acid. Theoretical amount required 4.94 ml of 0.05 M $K_3Fe(CN)_6$.

Effect of pH on Oxidation of Cobalt in a Glutamic Acid Medium. The bright red colored complex of cobalt with glutamic acid is formed over a fairly wide pH range. It is oxidized to a violet colored complex even at ordinary temperatures. The course of the oxidation reaction was followed quantitatively by titrating about 15 mg Co^{2+} with 0.05 M potassium ferricyanide, titration was carried out in 50 ml of 0.2 M glutamic acid at a definite pH. Fig. 2 shows the course of the reaction. Titration can be carried out over the pH range 4.3-12.5. At a pH greater than 7 partial separation of a precipitate occurs, while in solutions with pH greater than 12.5 it becomes impossible to establish the position of the titration end point. At pH values greater than 11.5, after about 15 min, the color of the solution gradually starts to change and a brown color appears.

It is clear from Fig. 2 that as the pH increases the initial potential of the solution starts to decrease gradually. On Curve 1 there is observed a further potential drop after the first addition of potassium ferricyanide solution. Quantitative oxidation occurs over the pH range 9.8-11.4. The potential is readily established in all cases in the immediate neighborhood of the titration end point (within 2 min), independently of the pH. The potential jump at the end point does not change strongly, but is strong enouth to establish the titration end point reliably.

At pH's within the optimum range there is no need to protect the solution being titrated from contact with atmospheric oxygen (Fig. 3). Even after solution has been allowed to stand for 3½ hours, oxidation of cobalt is negligible.

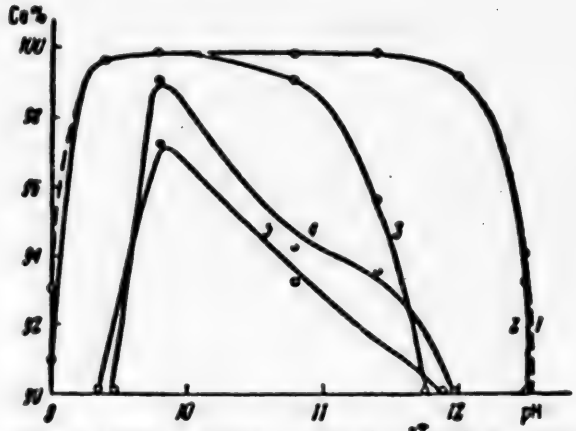

Fig. 3. Titration of the complex of Co^{2+} with glutamic acid in the absence and in the presence of atmospheric oxygen. 1) Immediately in an inert atmosphere; 2) immediately in air; 3) in the air after 3.5 hr; 5) in the air after 5 hr; 5) in the air after 12 hr.

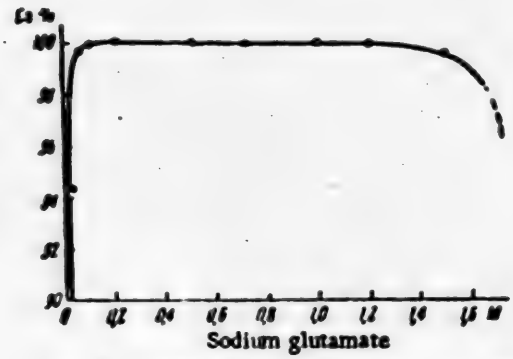

Fig. 4. Effect of glutamic acid concentration on oxidation of divalent cobalt with potassium ferridyanide; 4.5×10^{-3} M Co^{2+} solution was titrated with 0.05 M $K_3Fe(CN)_6$ at pH 10.4 in a volume of 55 ml.

Effect of Glutamic Acid Concentration. Even in the presence of a tenfold amount (with respect to cobalt) of glutamic acid, the potential change at the titration end point is only 2-3 mv for 0.1 ml of $K_3Fe(CN)_6$. As the amount of glutamic acid used increases so does the potential jump. When the amount of glutamic acid is 40-240 times as much as that of the cobalt the potential changes by 20-50 mv on addition of 0.1 ml of ferricyanide solution.

When very large amounts of glutamic acid are used (more than 250-fold) low results are obtained for cobalt (at pH 10.4, Fig. 4).

Under the optimum conditions, i.e., at pH 9.8-10.4 and a glutamic acid concentration of 0.2 M, and using a volume of 50 ml of solution, it is possible to determine 1.5-50 mg of cobalt with reasonable accuracy (Table 1). At higher cobalt concentrations it is necessary to increase the amount of glutamic acid.

Effect of Other Ions. Chlorides, nitrates, and sulfates in amounts which are 50-100 times that of cobalt do not affect the results of cobalt determination. A number of cations form colorless (Mo^{VI}, Bi^{3+}, Zn^{2+}, Mn^{2+}) or colored (Fe^{3+} intense yellow-red, Cu^{2+} intense bluish-violet, VO_3 bright yellow, Ni^{2+} intense blue) compounds with glutamic acid, but even when these elements are present in large amounts they do not affect the results of cobalt determination (Table 2); the exception is manganese.

TABLE 1. Titration of Divalent Cobalt in a Glutamic Acid Medium with Potassium Ferricyanide Solution (pH 9.8-10.4, mean of three determinations)

Co taken, mg	Co found, mg	Co taken, mg	Co found, mg
1.45	1.39*	14.52	14.52**
2.90	2.85*	21.80	21.80**
7.26	7.26**	29.00	29.00**

* Titrated with 0.01 M $K_3Fe(CN)_6$.
** Titrated with 0.05 N $K_3Fe(CN)_6$.

When manganese compound is added on its own to a glutamic acid solution (pH 10.4), as soon as the first drop of $K_3Fe(CN)_6$ solution is added, a greenish-brown colored precipitate appears, and the measured potential value corresponds to the potential value of the system $Fe(CN)_6^{3-}$ / $Fe(CN)_6^{4-}$. When, however, the solution contains cobalt as well as manganese, the precipitate of the manganese compound only appears after complete oxidation of divalent cobalt. The compound of manganese with glutamic acid is not oxidized by atmospheric oxygen, in contrast to the compound of manganese with glycine [7]. Quantitative results were obtained for cobalt in the presence of 1.5 times its amount of manganese.

Determination of Cobalt in Steel. About 0.5 g of steel containing Cr, Mo, W, and V in addition to cobalt is dissolved in perchloric acid and the solution evaporated almost to dryness. The residue is dissolved in distilled water containing a small amount of perchloric acid and the liquid heated to separate the tungstic acid. Solution and precipitate are transferred to a 100-ml standard flask and the volume made up to the mark with distilled water. 25 ml of 60% glutamic acid solution (pH 10.1-10.5) is added to 25 ml of this solution and the final solution titrated

TABLE 2. Determination of Cobalt in the Presence of Other Metals (14.52 mg of Co was titrated with 0.05 M $K_3Fe(CN)_6$ in 50 ml of solution in a 0.2-1.5 M glutamic acid medium, pH 10.1-10.4)

Taken, mg		Co found, mg	Error, %	Molar concentration of glutamic acid
Ni^{2+}	—	14.53	+0.07	0.2
	14.6	14.52	0	0.2
	58.4	14.53	+0.07	0.2
	116.8	14.45	−0.48	0.2
	101.3	14.50	−0.14	0.75
	202.6	14.51	−0.07	1.5
Cr^{3+}	10.288	14.53	+0.07	1.5
	20.567	14.50	−0.14	1.5
	51.42	14.35	−1.17	1.5
	102.80	14.20	−2.2	1.2
Cd^{2+}	140.3	14.49	−0.21	1.2
	280.5	14.42	−0.69	1.2
	280.5	14.51	−0.07	1.5
	561.0	14.28	−1.67	1.2
Al^{3+}	13.42	14.52	0	1.2
	33.55	14.35	−1.17	1.2
	67.10	14.35	−1.17	1.2
Fe^{3+}	139.85	14.48	−0.28	1.2
	139.85	14.53	+0.07	1.5
	279.7	14.47	−0.34	1.5
Cu^{2+}	191.0	14.51	−0.07	1.5
	382.0	14.50	−0.14	1.5
Zn^{2+}	162.5	14.52	0	1.2
	325.0	14.49	−0.21	1.5
W^{VI}	46.0	14.52	0	0.75
	460.0	14.49	− 0.21	0.75
	920.0	14.40	− 0.83	1.5
Bi^{3+}	51.8	14.52	0	0.75
	258.3	14.47	− 0.34	0.75
	518.0	14.45	− 0.48	0.75
	1036	14.54	+ 0.14	1.5
Ti^{IV}	9.99	14.49	− 0.21	0.5
	4.99	14.51	− 0.07	0.5
Mo^{VI}	3360	14.45	− 0.48	0.75
	1680	13.30	− 1.51	0.5
	504	14.51	− 0.07	0.5
	840	14.49	− 0.21	1.5
	840	1.33	−70.7	0.25
VO_3^-	6.10	14.52	0	0.5
	21.8	14.57	+0.342	0.5
	109.0	14.57	+0.21	0.5
As^V	141.2	14.55	+0.21	0.5
	282.4	14.51	−0.07	0.5
Mn^{2+}	5.48	14.53	+0.07	0.5
	8.22	14.51	−0.07	0.5
	13.70	14.49	−0.21	0.5
	27.40	14.55	+0.21	1.1
	68.5	14.33	−0.82	1.1

potentiometrically with 0.05 M potassium ferricyanide solution. The mean cobalt content from several determinations was found to be 4.15% (amount that should be present, 4.52%). In another steel the cobalt content found was 2.05%, the amount that should be present being 1.95%.

Determination of Cobalt in an Ore. About 1 g of finely ground arsenic sulfide ore (Co, Ni, As) is dissolved in perchloric acid and the solution evaporated to dryness; the residue is dissolved in water containing a few drops of sulfuric acid. The evaporation process is repeated and the solution transferred with water containing a few drops of perchloric acid into a 250-ml standard flask, water being added to bring the volume up to the mark. To 25 ml of the solution obtained as is added 25 ml of 60% glutamic acid solution (pH 10.5), and the cobalt is titrated potentiometrically with 0.1 M $K_3Fe(CN)_6$. As the result of a large number of determinations the mean cobalt content of a sample which was supposed to contain 0.66% was found to be 0.67%.

On the basis of a large number of determinations carried out on a cobalt-nickel ore, the mean cobalt content found was 0.56% Co as against an expected content of 0.51% Co.

SUMMARY

The quantitative oxidation of divalent cobalt as the divalent cobalt complex of glutamic acid by means of potassium ferricyanide has been studied potentiometrically as a function of pH, glutamic acid and cobalt concentrations. It has been found that the cobalt (II)-glutamic acid compound is stable in air at pH 9.8-11.4, and it is possible to oxidize it quantitatively with potassium ferricyanide. As a result of the studies carried out, a method has been developed for the determination of cobalt in various materials (steels, ores). The method permits determination of 1% Co in zinc, nickel, bismuth, cadmium, copper, and molybdenum. Manganese in amounts which are five times that of cobalt does not interfere.

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NITROPHENYLHYDRAZONES OF ISONITROSOACETOPHENONE AS SENSITIVE AND SELECTIVE REAGENTS FOR COBALT*

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Isonitrosoacetophenone has been used for a long time as a reagent for detecting iron [1-3], cobalt, nickel, cadmium, copper, lead, tin, zinc, and mercury [4]. With these elements the reagent forms inner-complex salts with characteristic colors. Recently, the p-nitrophenylhydrazones of certain isonitroso compounds (e.g., isonitrosoacetone and 3-isonitrosopentanedione [5] were suggested as selective reagents for cobalt. A hydrazone is readily formed as the result of the presence of a free keto group in isonitrosoacetophenone. It was of interest to study the effect of the introduction of an aromatic group on the reactivity of the group for cobalt. In this connection we synthesized the p-nitro- and 2,4-dinitrophenylhydrazones of isonitrosoacetophenone and studied their analytical behavior.

Synthesis of Reagents. a) p-Nitrophenylhydrazone of isonitrosoacetophenone. 1.5 g of p-nitrophenylhydrazine in 100 ml hot water was added to a solution of 1.5 g of isonitrosoacetophenone (chemically pure grade, Theodore Shuchardt) in 25 ml of hot water. The mixture was acidified by addition of a few drops of glacial acetic acid and was kept on a boiling water bath for 25-30 min. After cooling, the orange precipitate was filtered off; it was recrystallized from methanol. The preparation obtained was a dark-orange powder with m.p. 212°. Analysis **:

Found (in %):	58.78 C;	4.39 H;	18.85 N.
$C_{14}H_{11}N_4O_3$. Calculated (in %):	59.15 C;	4.23 H;	18.72 N.

b) 2,4-Dinitrophenylhydrazone of isonitrosoacetophenone. Equimolar amounts of isonitrosoacetophenone and 2,4-dinitrophenylhydrazine were mixed in hot dilute alcohol, and the mixture was acidified with acetic acid and heated under reflux for 3-4 hr. On cooling, a dark-red precipitate was obtained. The precipitate was recrystallized from toluene. The preparation obtained was a red crystalline powder with a m.p. of 233°. Analysis:

Found (in %):	51.28 C;	3.25 H;	20.50 N.
$C_{14}H_{10}N_5O_5$. Calculated (in %):	51.06 C;	3.34 H;	21.28 N.

Detection of Cobalt. A 0.1% solution of the reagents in ethanol was used.

To one drop of test solution contained in a micro test tube was added one drop of concentrated ammonia and two drops of the alcoholic solution of the reagent. Depending on the amount of cobalt, a dark or light violet color develops. When very small amounts of cobalt are present a rose color develops, and in such cases the color is observed after removing excess unreacted reagent by extraction with ether.

When the p-nitrophenylhydrazone of isonitrosoacetophenone is used the limit of identification is 0.1 μg, while the limiting dilution is 1:2 000 000. When the 2,4-dinitrophenylhydrazone of isonitrosoacetophenone is used, a dark-red color appears; the limit of identification is 0.25 μg Co, while the limiting dilution is 1 : 1 000 000.

Nickel at high concentrations gave a light-blue color, which can be eliminated by addition of a dilute solution of an alkali metal cyanide. A large excess of cyanide should be avoided since it interferes with cobalt detection. Other cations which form soluble ammines, e.g., silver, copper, and palladium, did not give a color with the reagents. The color which develops in the presence of cobalt was stable in the presence of a moderate excess of KCN and ammonium salts.

* Translated from English by Z. L. Podgaiskaya.

** Analysis was carried out by Doctors Wiler and Straus (Oxford, England).

Cadmium, iron, lead, manganese, mercury, tin, and zinc (they give color reactions with isonitrosoacetophenone) do not interfere with cobalt detection.

Both reagents are soluble in solutions of the alkali metal hydroxides, since they are enolizing nitroso compounds, to form acidonitro compounds as a result of a regrouping. Both reagents also possess acid properties since they contain an oxime group with a hydrogen atom which is capable of forming a coordination bond with nitrogen. The transformation into the ionogenic quinoid form, which is soluble in alkalis, can be explained in the same way as in the case of the p-nitrophenylhydrazones of isonitrosoacetone and 3-isonitrosopentanedione [5].

This regrouping does not proceed fully enough in the presence of ammonia, so that only a bright-orange color developed.

When cobalt and ammonia are present, regrouping of the reagent molecules occurs with simultaneous complexing of cobalt as a chelate compund.

Formation of the violet complex compounds of cobalt with the p-nitro- and 2,4-dinitrophenylhydrazones of isonitrosoacetophenone, which are stable to alkali metal cyanides, can be used as a new and fairly sensitive reaction for cobalt. The ordinary cations do not interfere. The introduction of the phenylhydrazone group into isonitrosoacetophenone essentially modifies the nature of the reagent, as a result of which a new, selective reagent for cobalt is obtained.

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SUMMARY

p-Nitro- and 2,4-dinitrophenylhydrazones of isonitrosoacetophenone are suggested as specific and sensitive reagents for cobalt. A deep violet colored complex is formed with the former, while a deep red color is given by the latter reagent. Interference from nickel is supressed by addition of potassium cyanide. The limits of identification are 0.1 and 0.25 μg of cobalt respectively, while the dilution limits are 1 in 2 000 000 and 1 in 1 000 000 respectively.

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DETECTION OF BORON IN SILICATE ORES BY A TRITURATION METHOD

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During qualitative detection of boron by combustion as volatile methyl borate [1], or in the form of its fluoride [1], compounds of copper, barium, and some other elements color the flame green [2,3]. Detection of boron with curcumin [2,4,5,6] is difficult in the presence of hydrochloric acid solutions of zirconium, titanium, and molybdenum, and also in the presence of oxidizing agents. Oxidizing agents and fluorides interfere with the use of chromotrope 2B (sodium p-nitrobenzene-azo-2-chromotropate)[6]. Detection of boron with quinalizarin suffers from the same defects when preliminary decomposition is effected by fusion with Na_2CO_3. According to Isakov [7], oxidizing agents (nitrates, chromates, and hydrogen peroxide) and colored ions (trivalent iron, copper, cobalt, tri- and sexivalent chromium, quinquevalent vanadium, and sexi- and septivalent manganese) interfere with detection of boron by means of quinalizarin. Isakov has suggested detection of boron by triturating the ore to be tested with quinalizarin in the presence of 1-2 drops of sulfuric acid. By using this technique it was found possible to limit the effect of interfering impurities and to increase the sensitivity of detection.

The aim of the work described here was to establish the optimum conditions for carrying out this reaction, and to determine its sensitivity for complex borosilicate ores (different modifications of datolite, danburite, and axinite). The chemical composition of the ore samples tested are given in Table 1.

TABLE 1

Rock	Chemical composition, %									
	B_2O_3	SiO_2	Al_2O_3	FeO	Fe_2O_3	CaO	MgO	MnO	loss on calcining	total
Varieties of datolite										
a) Quartz-carbonate	15,90	37,35	None	2,23	1,31	34,4	0,20	0,66	7,48	99,33
b) Garnet	8,93	37,18	0,19	1,08	13,71	34,7	0,39	0,44	3,18	99,80
c) Hedenbergite	8,77	43,32	None	8,05	None	29,20	5,51	1,70	3,35	99,90
d) Hedenbergite-garnet	9,60	40,87	1,92	4,35	6,15	31,00	2,44	0,85	3,60	100,76
Magnetic iron ore	0,14	7,63	2,40	23,79	64,20	0,65	0,22	0,25	None	99,28
Danburite	26,30	26,30	0,30	None	0,40	22,85	0,28	None	0,04	99,97
Axinite	5,72	41,27	18,70	2,90	1,18	21,68	0,26	8,10	0,51	100,32

The experimental technique consisted in the following: An aliquot of ore (40-6 mg) was triturated, first without quinalizarin in order to give the greatest reaction surface, and then with quinalizarin, the total trituration taking not more than 30 sec. One drop of concentrated sulfuric acid was added to the mixture. When the B_2O_3 content of the aliquot is 6 mg or more, the reaction goes in the cold; the ground mixture acquires a cornflower blue color. When an aliquot containing less than 6 mg of B_2O_3 is ground for a longer period, the color only appears after heating the ground mixture (until sulfur trioxide is evolved). All the samples tested gave a positive reaction for boron. The exception was the magnetic iron ore with a B_2O_3 content of 0.14%. The qualitative reaction for this material gave a noncharacteristic color, presumably because of formation of basic salts of trivalent and divalent iron with a brown color which mask and sorb the colored quinalizarin complex.

The color intensity depends on the boron content of the samples. For B_2O_3 contents greater than 8%, the color

TABLE 2

B_2O_3 concentration	B_2O_3 content of the test samples					Color after trituration
	datolite, quartz arbonate	datolite, garnet	datolite, hedenbergite	datolite, hedenbergite garnet	danburite	
Above ten percent, mg	15,90	—	—	—	26,30**	Cornflower blue
	4,8	—	—	—	0,52	
Between one and ten percent, mg	1,59*	8,93	8,77	9,00	1,80*	» »
	0,03	0,18	0,18	0,19	0,026	
Tenths of a percent, mg	0,8*, 0,4*, 0,2*	0,45*, 0,23*	0,44*, 0,22*	0,48*, 0,24*	0,9*, 0,45*, 0,22*	» »
	0,016; 0,008; 0,004	0,009 0,004	0,009 0,004	0,01, 0,005	0,013; 0,006; 0,003	
Hundredths of a percent, mg	0,1*	0,12*	0,11*	0,12*	0,11*	Violet
	0,002	0,002	0,002	0,0025	0,0015	

*The B_2O_3 content was lowered by mixing the ore with silica sand.

**B_2O_3 was determined in danburite without heating. The color of the reaction product was dark-cornflower blue.

TABLE 3

Test material	B_2O_3 content %	Detection of boron with quinalizarin after:	
		Fusion with Na_2CO_3	Trituration
Hedenbergite	0.5	Not detd.	Detected
Wallastannite	1.10	" "	Ditto
Dark colored ore	0.67	" "	"
Lime with hedenbergite inclusions	0.18	" "	"
Silica schist	None	" "	Not detected

of the reaction products after trituration is dark blue; at lower B_2O_3 contents the color intensity is weaker.

In order to establish the reaction sensitivity, samples containing boron were mixed with ground amorphous silica, and powders were prepared in this way which contained very small amounts of B_2O_3. All these powders after trituration with quinalizarin and being treated with one drop of sulfuric acid gave positive reactions for boron after heating (they gave the cornflower blue color); they included mixtures containing down to 0.003 mg B_2O_3. Mixtures containing 0.002 mg B_2O_3 did not give the reaction. Results of experiments carried out to establish the sensitivity are given in Table 2. As these results show, the limit of identification is 3 μg of B_2O_3.

The sensitivity of the qualitative reaction for boron by the quinalizarin trituration method was tested out on various rocks and minerals after preliminary decomposition of the ore by fusion with Na_2CO_3. Silicate rock was fused on the lid of a platinum crucible with a small amount of Na_2CO_3 [1]. The melt was leached with water and the extract evaporated to dryness. A solution of quinalizarin in sulfuric acid was added to the residue and the mixture heated gently. When no interfering impurities were present, the violet color of the quanlizarin changed to blue in the presence of boron.

Comparative results are given in Table 3.

As the results in Table 3 show, after fusion with Na_2CO_3, boron could not be detected in the samples by means of quinalizarin, since the melts and their extracts had a dark-green color, which testified to the presence of large amounts of manganese in the samples.

It should be pointed out that after prolonged trituration (for more than one minute) the blue color may not even appear because of the formation of a large amount of colored reaction products which mask the color. Accordingly trituration should be not too vigorous and should be of short duration.

From the results given it is clear that the trituration method ensures higher sensitivity and reliability than the fusion method. Minerals which have varying lattice energies and lattice parameters are present in borosilicate rocks. Minerals with a low crystal lattice energy will be the first to be destroyed [8].

As an example we give below the composition and structure of minerals which accompany datolite, according to Betekhtin [9], and also the energy of their crystal lattices calculated by Fersman's method [10, 11].*

Mineral	−U, kcal/mole
Hedenbergite $CaFe[Si_2O_6]$	7593.7
Manganese-hedenbergite $CaMn[Si_2O_6]$	7563.0
Garnet	
grossularite $Ca_3Al_2[SiO_4]_3$	6992.7
andradite $Ca_3Fe_2[SiO_4]_3$	6043.9
Datolite $Ca_2B_2[SiO_4][OH]_2$	5567.5
Calcite $CaCO_3$	648

On the basis of the results on the energies of the crystal lattices of silicate minerals, it follows that hedenbergite will be the hardest to break down from silicates, and datolite the easiest. It is also obvious that these minerals will dissolve in sulfuric acid at the same relative rates. In fact, Berlin [12] has demonstrated experimentally that the rate and extent of dissolution of minerals which compose datolite ore are not the same: datolite mineral is decomposed most rapidly and completely, and decomposes to the extent of 96-100% in 60 min; garnet decomposes to the extent of 12-20% in the same period, hedenbergite decomposes to the extent of 2-4%, and calcite 47-50%. The slow rate of dissolution of calcite can be explained by formation of a sparingly soluble film of gypsum on its surface.

* Where possible, calculations were based on the eka complex anions.

Accordingly, during trituration of datolite ore the first of the silicate minerals to be broken down and to dissolve in sulfuric acid will be the mineral datolite, so that the boric acid will dissolve, while the interfering impurities (manganese, iron) will remain in the solid phase. This is the reason for the high sensitivity of the triturating method of detecting boron in datolite ore, and for the weak interference from impurities.

It should be noted that the reactivity of various borosilicates and the sensitivity with which boron can be detected in them will also depend on the energy of the crystalline lattice.

Mineral	–U, kcal/mole
Axinite $Ca_2[Mn, Fe]Al_2BSi_4O_{15}[OH]$	7785.4
Datolite $Ca_2B_2[SiO_4]_2[OH]_2$	5567.5
Danburite $Ca[B_2Si_2O_8]$	4930.0

Boron is detected with the greatest difficulty in the mineral axinite and is most readily detected in danburite. The limit of identification for axinite is 30 μg, for datolite 3 μg and for danburite less than 3 μg.

SUMMARY

Boron can be readily detected in borosilicate ores (in various species of datolite and in danburite) by triturating them with quinalizarin and then treating the mixture with 1-2 drops of sulfuric acid.

It has been shown that the reactivity of borosilicates and the limit of identification depend on the lattice energies of the minerals composing the ore.

The optimum conditions for detecting boron are gentle and brief trituration (not more than 30 sec) followed by heating of the reactants until sulfur trioxide fumes are evolved.

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CHROMATOGRAPHIC SEPARATION OF HALIDE IONS

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Development of chromatographic methods of separating anions became possible after strongly unifunctional anion exchange resins became available [1]. Quantitative separation of fluoride, chloride, bromide, and iodide anions is a fairly difficult analytical problem; development of rational chromatographic methods of separating them is accordingly desirable [2]. Insufficient work has been carried out along these lines hitherto. Equilibrium absorption of binary mixtures of chloride-bromide ions and bromide-iodide ions by chromatographic grade alumina has been studied under static conditions [3]. Rieman and Lindenbaum [4] have separated mixtures of potassium chloride and bromide on the strongly basic anion exchange resin Amberlite XE-67 in the nitrate form. The work carried out by Attebery and Boyd is the only one in which a study was made of the chromatographic separation of mixtures of fluoride, chloride, bromide, and iodide ions; separation of a mixture of the ammonium halides on the anion exchange resin Dowex-2 in the nitrate form was, however, not completely quantitative.

We thought that the use of cation exchange resins for separating anions by partition chromatography might be a promising approach. The use of cation exchange resins for this purpose should be based on a study of the distribution of the components of an aqueous-organic mixture between the ion exchange resin phase and the solution, and also on a study of the partition coefficients of the materials being separated between both phases.

EXPERIMENTAL

Cation exchange resin SBS containing 70% styrene was prepared by sulfonating a butadiene-styrene vulcanizate containing 3 parts by weight of combined sulfur and 100 parts by weight of the copolymer with 95% sulfuric acid for 10 hr at 100°. The exchange capacity of the cation exchange resin with respect to sodium chloride proved to be 3.43 mg-equiv per g of dry ion exchange resin. The degree of swelling of the ion exchange resin in the H and in the Na forms was 2.35 and 2.05 g per g of dry resin respectively.

A study was made of the distribution of the components of aqueous-methanol and aqueous-aceton mixtures* between the cation exchange resin in the hydrogen and sodium forms and the binary solutions, throughout a whole range of compositions of the binary solutions.

First, the swelling of both forms of the resin in binary mixtures of varying composition was studied by a technique given in [6]. The swollen resin was brought to an "surface dry" state by centrifuging in a beaker with a grid bottom; an accurately weighed aliquot of the centrifuged resin was then brought to constant weight in a weighing bottle at 105°.

In order to study the distribution of the components of the binary solution, an accurately weighed aliquot of about 1 g was placed in a 25-ml bottle with a well-fitting ground glass stopper, and 15 ml of a binary solution of known composition poured into the flask; the moisture content of the ion exchange resin was taken into account in preparing the binary solution. After 24 hours the solution was replaced by 15 ml of a solution with the initial composition. This operation was repeated until the composition of the solution found in equilibrium with the ion exchange resin became equal to the original composition of the solution, which was usually expressed by a round number for the molar fraction of the nonaqueous component.

In order to determine the composition of the binary solution in the resin phase, the latter was brought to a surface dry state by centrifuging, and part of this resin was transferred to a tared bottle containing 40 ml of water. The increase in weight of the bottle is equal to the weight of swollen resin, and since the degree of swelling as a function of the composition of the quilibrium solution has already been studied, the weight of dry resin introduced into the bottle was also known.

* Absolute methanol and acetone were prepared according to [5].

It was established experimentally that the nonaqueous component is quantitatively extracted from the ion exchange resin phase in one extraction. The concentration of this component was determined on a liquid interferometer using a calibration curve constructed beforehand.

The difference between total swelling and content of nonaqueous component is equal to the water content of the aliquot of resin taken. The composition of the solution in the resin phase was expressed as molar fractions of the nonaqueous component. The results obtained N_2I are plotted as a function of the molar fraction of the nonaqueous component in the equilibrium binary solution N_2; four of the systems studied are shown in Fig. 1.

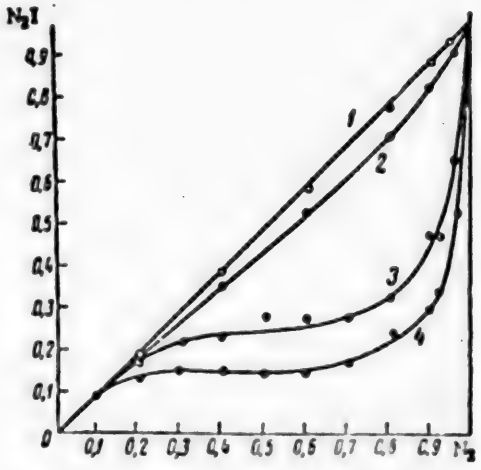

Fig. 1. Molar fraction of nonaqueous component in the resin phase (N_2I) as a function of the molar fraction of this component in the solution phase (N_2). 1) Water-methanol-resin in the H form; 2) water-methanol-resin in the Na form; 3) water-acetone-resin in the H form; 4) water-acetone-resin in the Na form.

The figure clearly shows that the components of the aqueous-methanolic mixtures are distributed almost uniformly between the resin phase and the binary solution phase. This is especially the case for the resin in the hydrogen form, for which the partition curve of the components almost fuses with the diagonal of the $N_2I - N_2$ square. Aqueous-acetone mixtures are distributed unevenly between both phases. Asymmetry is particularly clearly marked for the resin in the sodium form (Curve 4). It is clear from Fig. 1 that the Na ion exchange resin phase which is in equilibrium with the solution, and whose molar fraction of acetone is 0.7, contains 82 mole percent of water. This fact means that it should be possible to realize efficient partition chromatography on the carrier – the ion exchange resin in the sodium form containing the aqueous-acetone mixture with a predominating water content as the stationary phase, and a mobile phase in which acetone predominates.

In order to study the partition of sodium halides between the phases, analytical grade reagents which were not subjected to further purification were used. To flasks containing an aliquot of air-dry resin corresponding to 2 g of the dry resin was added acetone and water in such amounts that after taking into account the water content of the resin and its degree of swelling with respect to water and acetone, 15 ml of a solution of a given composition was obtained. Varying amounts of sodium halide corresponding to variations in salt concentration over the range 0.05 to 1.0 mg/ml were then added to these flasks. Experiments were carried out at 22° for 24 hr with periodic shaking. Special experiments established that this period was in excess of that required to establish equilibrium distribution of the salts between both phases. Next, 10 ml of the equilibrium solution was evaporated on a water bath at 100°; the dry residue was dissolved in 10 ml of distilled water and the salt concentration of the solution obtained determined on an interferometer using calibration curves which were constructed beforehand for all the halides. The salt content of the resin phase was determined by the difference between its content in the original and equilibrium solutions. On the basis of the results obtained, a partition isotherm was constructed within the coordinates salt concentration in the resin phase vs. salt concentration in the equilibrium solution. The concentration was expressed in both phases as mg/ml* Over the halide concentration range studied the partition lines are completely linear, as is evident, e.g., from Fig. 2 in which are shown the partition isotherms for solutions of NaCl and NaBr for a molar fraction of 0.7 of acetone in the external solution.

* The volume of the solution in the swollen resin phase was calculated on the basis of data on the densities of aqueous-acetone mixtures [8].

Partition Coefficients

Salt	Solubility, g/100 ml water	N_0	K	Salt	Solubility, g/100 ml water	N_0	K
NaI	178,7	0,8	2,05	NaCl	36,0	0,7	7,90
NaBr	90,5	0,8	9,0	NaCl	36,0	0,5	3,45
NaBr	90,5	0,7	2,65	NaF	4,2	0,5	11,1

A summary of the results obtained for the partition coefficients are given in the table; they are equal to the slopes of the partition isotherms.

The table shows that the salt which is most soluble in water (NaI) has the lowest partition coefficient, and vice versa. This is explained by the fact that the lower the solubility of a salt, the more strongly pronounced is the decrease in solubility produced by addition of acetone. It is also clear from the table that for a molar fraction of acetone in the equilibrium solution of 0.8, the partition coefficients of NaI and NaBr differ by 6.95 units; at a molar ratio of 0.7 for acetone the partition coefficients of NaBr and NaCl differ by 5.2 units, and for a molar ratio of 0.5 for acetone the partition coefficients of NaCl and NaF differ by 7.6 units. Such differences in the values of the partition coefficients are quite sufficient for a clear separation of mixtures by partition chromatography [7]. Accordingly, mobile phases with molar fractions of 0.8, 0.7, and 0.5 respectively of acetone were used for separating NaI, NaBr, and NaCl. Bearing in mind the very low solubility of NaF in mixtures containing much acetone, in order to compress its zone this material was eluted with a mixture containing 30% acetone.

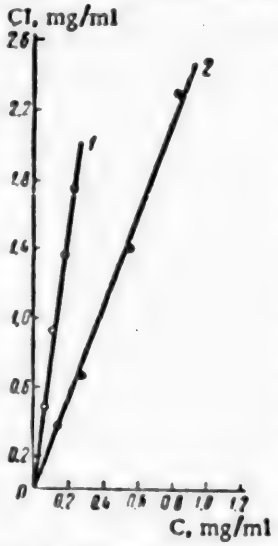

Fig. 2. Partition isotherms. 1) NaCl and 2) NaBr at a molar ratio of 0.7 of acetone.

A 50 × 2 cm column contained 32 g of the ion exchange resin in the sodium form (particle size 0.25-0.50 mm) swollen in a mixture containing 80% acetone. The halides were introduced into the top part of the column in the form of a mixture of the solid salts. The throughput of the mobile phase (0.5 ml/min) was kept constant by means of a Mariott flask provided with a narrow capillary. Ten-ml aliquots of eluate were collected and each aliquot analyzed on an interformmeter as described during the study of the partition coefficients. Elution curves obtained during separation of the four halides in a typical experiment are shown in Fig. 3.

15.0 mg NaI, 20.2 mg NaBr, 15.0 mg NaCl, and 20.0 mg NaF were introduced into the column. On the basis of the areas under the peaks on the elution curves, the values obtained for the respective salts were 14.9, 19.8, 15.0 and 20.2 mg. Thus separation is strictly quantitative, the error not being greater than 1%. Not only do the zones not overlap each other (as observed previously [1]) but there are clear gaps between the zones, the value of which is determined by the time taken to replace one mobile solvent by the next. The elution curves are arranged in order of increasing partition coefficient, no tailing is observed, and the curves are almost ideal Gaussian error curves. It follows therefore that our experiments are covered by the theory of partition chromatography, and are not complicated by side effects.

By varying the degree of cross-linking of the resin, and also the nature and composition of the binary solutions, it is possible to change the partition coefficients of the materials to be separated very accurately and over extremely wide limits. The

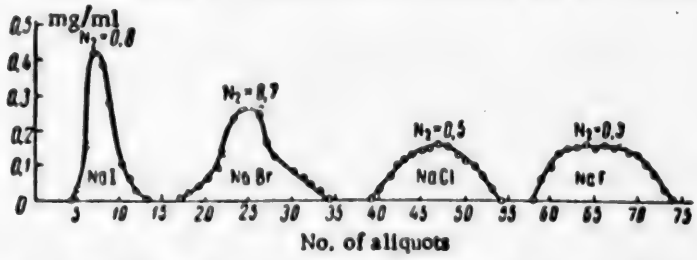

Fig. 3. Elution curves of Na halides. N_2 is the molar fraction of acetone in the mobile phase.

method outlined here therefore can be widely applied to the development of chromatographic methods of separating complex mixtures of anions.

SUMMARY

A study has been made of the partition of the components of aqueous-methanol and aqueous-acetone mixtures between the cation exchange resin SBS in its hydrogen and sodium forms and the binary solutions, over a whole range of varying compositions of the binary solutions.

The partition coefficients of sodium halides between the resin in its sodium form and aqueous-acetone mixtures have been studied.

On the basis of the results obtained a method has been developed for the quantitative chromatographic separation of mixtures of sodium halides.

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SIMULTANEOUS DETERMINATION OF HYPOCHLORITES, CHLORITES, AN CHEORATES BY MEANS OF ARSENITE, USING OsO_4 AS CATALYT

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Little work has been carried out on the titrimetric determination of oxygen compounds of chlorine in each other's presence; a review of this work is given in [1]. Almost all these methods are based on stepwise titration by means of various solutions of separate aliquots of one or more components, depending on the conditions. In the present article the possibility is demonstrated of carrying out a titrimetric determination of hypochlorites, chlorites, and chlorates by means of arsenite on one aliquot.

The hypochlorite solutions were prepared by neutralizing excess of an alkali solution of hypochlorous acid, obtained from Cl_2O formed by the interaction of yellow mercury oxide with chlorine in CCl_4 [2]. Chlorite solutions were prepared by the interaction of ClO_2 solutions, obtained from potassium chlorate, oxalic and sulfuric acids [3], with excess alkali in the presence of hydrogen peroxide [4]. A bicarbonate solution of sodium arsenite was used for titration.

An A4-M2 tube voltmeter was used for the potentiometric titration of hypochlorites and chlorites. The indicator electrode was a smooth platinum disc, while the reference electrode was a saturated calomel electrode with an agar-agar bridge filled with saturated potassium chloride solution. The solution being titrated was stirred with a magnetic stirrer. The end point was determined on the basis of the maximum value of $\Delta E/\Delta C$.

Control analyses were carried out by other methods: hypochlorite, chlorite or their total amount was determined iodometrically [5], while chlorate was determined bromatometrically [6].

a) Determination of Chlorites by Means of Arsenite. Chlorites are very slowly reduced by arsenite in alkaline media [1, 7]. We have found that this process can be speeded up considerably in the presence of OsO_4. Characteristically, osmic acid is a good catalyst of many oxidation-reduction reactions [8-10], and, moreover, is used during the titrimetric determination of chlorates [11-13].

We attempted to develop a potentiometric method for determining chlorites with arsenite in the presence of OsO_4. As preliminary experiments showed, such a method is possible, the accuracy and speed of titration of chlorites being dependent on a number of factors.

Since chlorite solutions as a rule contain some chlorates, determination of chlorites must be carried out in an alkaline medium, since in acid solutions in the presence of OsO_4 reduction of chlorates is possible [8-13]. It was established that when the chlorite solution to be titrated was made alkaline with sodium hydroxide, normally only hot solutions are titrated. Moreover, when solutions are made alkaline, it is impossible to titrate even hot solutions of the chlorites of the alkaline earth metal (in particular the chlorites of strontium and barium); this is most probably the result of catalyst deactivation.

Titration is significantly improved and simplified by using sodium carbonate for rendering the test solution alkaline. A characteristic feature in this case is that the reaction between arsenite and chlorite in the presence of OsO_4 proceeds appreciably more rapidly, and titrimetric determination of chlorite becomes possible even at room temperature. By using Na_2CO_3 for alkalinification it is also possible to titrate the alkaline earth metal chlorites. In this case sodium carbonate precipitates the alkaline earth metals as their carbonates, the presence of the precipitates of which does not affect the catalyst activity.

Too large an excess of catalyst concentration must be avoided, since under such conditions the catalyst is itself reduced, and this inevitably affects the accuracy of chlorite determination. Accordingly, we used only 0.2 ml

TABLE 1. Determination of Chlorites Iodometrically and by the Arsenite Method

Expt. No.	Chlorite	Chlorite determined, meq		Deviation, %	Acid to the original solution	
		iodometrically	by the potentiometric arsenite method		1 M Na_2CO_3, ml	chlorate, meq
1	Sodium	1,793	1,793	0	2	—
2		1,793	1,793	0	10	—
3		1,793	1,791	−0,11	5	2,2
4		1,793	1,798	+0,27	3	13,2
5		1,793	1,790	−0,17	3	8,8
6		3,586	3,590	+0,11	4	—
7	Calcium	2,163	2,162	−0,05	2	—
8		2,163	2,161	−0,09	10	—
9		2,164	2,163	0	5	4,4
10	Strontium	2,147	2,149	+0,09	3	—
11		2,147	2,150	+0,14	10	—
12		2,147	2,148	+0,05	5	8,8
13	Barium	2,145	2,147	+0,09	5	—
14		2,145	2,145	0	5	11,0

(4-5 drops) of a 0.1% solution of OsO_4 for each determination. This negligibly small amount of catalyst has almost no effect on the accuracy of a determination; it is sufficient, however, to speed up the reaction.

Table 1 contains results for titration of chlorites (10-20 ml) obtained with the new method of titrating with 0.1 N arsenite solution in the presence of OsO_4; these results are compared with those obtained by the usual iodometric method [5].

As the results in Table 1 show, chlorites can be titrated fairly accurately. It should be pointed out that when the test solution is made alkaline with sodium carbonate, neither the accuracy nor the speed of potentiometric titration drop even when a large excess of carbonate is used. The presence of even large amounts of chlorate has almost no effect on the accuracy of chlorite determination (see Table 3).

TABLE 2. Determination of Hypochlorites by the Iodometric and Arsenite Methods

Expt. No.	Hypochlorite	Hypochlorite determined		Deviation, %	Added to the original solution		
		iodometrically	by the potentiometric arsenite method		1 M Na_2CO_3, ml	1 N NaOH, ml	chlorite, meq
1	Sodium	1,252	1,250	−0,16	5	—	—
2		1,252	~1,36	>+8	5	—	8,97
3		1,252	1,254	+0,16	—	3	2,99
4		1,252	1,250	−0,16	—	10	8,97
5		1,252	*	—	—	3	8,97
6	Calcium	1,828	1,828	0	—	—	—
7		1,828	1,833	+0,28	5	—	—
8		1,828	1,828	0	—	10	10,82
9		1,828	*	—	—	3	10,82
10	Strontium	1,185	1,184	−0,09	—	—	—
11		1,185	1,184	−0,09	—	10	—
12		1,185	1,185	0	—	5	10,74
13		1,185	*	—	—	2	10,74
14	Barium	1,638	1,639	+0,06	—	—	—
15		1,638	1,638	0	5	—	—
16		1,638	~1,74	>+6	5	—	2,84
17		1,638	1,636	−0,12	—	5	—
18		1,638	1,638	0	—	3	2,14
19		1,638	1,638	0	—	10	12,84
20		1,638	*	—	—	3	12,84

* Solutions yellowed during titration (ClO_2 evolved); the end point could not be determined.

b) Determination of Hypochlorites by Means of Arsenite. In the given instance the most suitable method would appear to be a potentiometric determination of hypochlorites in an alkaline medium (pH > 9) by the method of Flis and Bynyaeva [7]. Their paper, however, does not contain any actual data on the amount of chlorite present, and there is no mention of titration of alkaline earth metal hypochlorites. Accordingly, we carried out several additional potentiometric determinations of hypochlorites in which the effects of alkalinification and the presence of chlorate in the test solutions were examined. The experimental results obtained during t ation of hypochlorites (10-20 ml) with 0.1 N arsenite solution are given in Table 2; these results are compared with those obtained by the cited iodometric method.

As the results in Table 2 show, during titration of hypochlorites with arsenite some characteristic features are observed.

Firstly, titration of hypochlorite in the absence of chlorite can be carried out whatever method is used for alkalinification. When, however, chlorite is present, alkalinification of test solution with sodium carbonate leads to sharp increase in the results for hypochlorite (Table 2, expts. 2 and 16). We think that this can be explained by the fact that the carbonate medium favors interaction of arsenite with chlorite.

Secondly, and this is the most important feature, with increasing chlorite concentration in the test solution, the solution must be made more alkaline with sodium hydroxide. As is evident from the results given in Table 2 (expts. 5,9,13,10) when the original alkalinity of the test solution is too low, potentiometric determination of hypochlorites in the presence of chlorites becomes impossible. When the solution is not alkaline enough, during titration with arsenite, chlorine dioxide starts to come off, and this colors the solution yellow; moreover, the pH of such solutions drops to 9 and lower.

c) Determination of Chlorates. For chlorate determination, we chose a bromatometric method based on titration with potassium bromate of the excess arsenite which has not reacted with chlorate [6]. This method, however, requires a solution in which the acidity is high (1 ml of concentrated HCl per 7 ml of solution), and prolonged boiling (15 min). These drawbacks are eliminated when OsO_4 is used [11].

As our experiments showed, when the test solution contains 0.2 ml of 0.1% OsO_4 solution, it is sufficient to acidity the test solution with 1-2 ml of concentrated HCl and to boil it for only 1-2 min.

d) Simultaneous Determination of Hypochlorite, Chlorite, and Chlorate. On the basis of our results given above and on published data, we concluded that by modifying the conditions it should be possible to determine hypochlorite, chlorite, and chlorate in one aliquot by meand of arsenite. Table 3 contains some experimental results characterizing such a determination of hypochlorite, chlorite, and chlorate in each other's presence when the method given below was used.

TABLE 3. Determination of Hypochlorites, Chlorites, and Chlorates in Mixtures

Expt. No.	Salt mixture	Determined, meq			Total in meq of hypochlorite and chlorite	
		hypochlorite	chlorite	chlorate	iodometrically	potentiometrically
1	Sodium	0,836	2,006	0,686	2,842	2,844
2		0,768	1,940	6,963	2,717	2,708
3		1,141	1,563	1,392	2,701	2,704
4		1,105	0,855	0,084	1,957	1,960
5		0,590	1,438	0,044	2,028	2,028
6	Calcium	1,098	0,840	0,064	1,942	1,938
7		2,230	1,761	0,111	3,991	3,991
8		0,716	1,220	0,859	1,931	1,936
9	Strontium	0,645	1,942	10,253	2,590	2,587
10		0,404	2,798	2,157	3,200	3,202
11	Barium	0,480	1,455	0,517	1,938	1,935
12		0,893	0,913	0,094	1,808	1,806

Determination of Hypochlorite. A known volume (10-20 ml) of test solution is alkalinified with 2-5 ml of 1 N sodium hydroxide solution. The platinum and calomel electrodes are immersed in the solution and the galvanic cell and tube voltmeter switched on. The test solution is stirred with a magnetic stirrer and titrated with arsenite solution, the potential changes being followed. Should the solution start to acquire a yellow color during titration, this may mean that the chlorite concentration is too high; determination should therefore be repeated after adding a larger amount of alkali (e.g., 10 ml of 1 N NaOH).

The arsenite is added dropwise near the end point. The end point is readily established on the basis of the maximum change in potential difference on addition of successive drops of arsenite solution, i.e., on $\Delta E / \Delta C$.

Determination of Chlorite. After hypochlorite determination, to the solution is added 1 N $NaHCO_3$ solution in an amount which is 1.5-2 times the amount of sodium hydroxide used (for converting the hydroxide to carbonate) and 4-5 drops (about 0.2 ml) of 0.1% OsO_4. At this stage the difference in potentials of the cell acquires its original value. Titration with arsenite is then continued as for hypochlorite determination until the potential jump corresponds to the end point. The concentration of the amount of chlorite is calculated from the amount of arsenite which has been used.

Determination of Chlorate. After the chlorite has been determined, the electrodes are removed from the solution and the chlorate determined bromatometrically in the same solution. For this purpose excess arsenite is added to the solution; the solution is neutralized to the methyl orange end point and then acidified with 1-2 ml of concentrated hydrochloric acid; about 0.1 g of KBr is finally added and the liquid boiled for 1-2 min. The excess arsenite is back titrated in the hot solution with bromate using methyl orange as indicator. The amount of chlorate is calculated on the basis of the difference between the amounts of original and residual arsenite.

SUMMARY

It has been established that OsO_4 catalyzes the reaction of chlorites with arsenite in an alkaline medium.

A new method has been developed for the potentiometric determination of chlorites in an alkaline medium by means of arsenite in the presence of OsO_4 as catalyst.

A new arsenitometric method is suggested for the successive determination of hypochlorites, chlorites, and chlorates in one aliquot.

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CONDITIONS FOR THE PHOTOMETRIC DETERMINATION OF FLUORIDE WITH ARSENAZO

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The basis of all photometric methods of determining fluoride is the process of complexing the cations of metals which have been complexed beforehand by some other reagent as a colored compound into colorless fluoride compounds. During this process the color intensity of the solution decreases. Other anions which form colorless complexes with the central ions of the metals can show similar behavior. The mechanism of the formation of colored complexes and their stability has not been studied sufficiently. Many authors have pointed out the significant influence of the acidity of the solutions and of certain ions on the sensitivity and accuracy of the results [1-4]; accordingly, it is recommended that standard experimental conditions must be strictly adhered to during fluorine determination.

The most suitable reagents for fluoride determination are those which form simple complexes over a wide pH range with metals. In the present article it is suggested that solutions of certain complexes of the reagent arsenazo can be used for determining fluoride; this reagent has been suggested by Kuznetsov [5] for the determination of small amounts of rare elements. The complex of arsenazo with thorium has already found application for the determination of fluoride [6]. Many arsenazo complexes posses an intense color, changes in which can be used for fluoride determination [7].

The complexes have a simple composition (the ratio of metal to reagent in them is 1:1 or 1:2) and exist over a wide pH range, so that they can also be used for altering the sensitivity of fluoride determination over a wide concentration range.

On adding fluorides to solutions of the colored complexes of arsenazo, some of the metal is complexed into a colorless fluoride complex, while part of the reagent changes to the free state. The optical density of solutions decreases at wave lengths characteristic of the complexes, and increases at wave lengths characteristic of the reagent. In Fig. 1 are shown as examples the change in the absorption spectra of solutions of the complex compounds of arsenazo with the uranyl ion on adding sodium fluoride to them at varying pH's. Fig. 2 shows the changes in the concentration of the colored complex under the action of fluoride at various acidities of the solutions.

Calibration curves for the determination of fluorine are shown in Fig. 3. Calibration curves were constructed as follows. One-ml lots of $5 \cdot 10^{-4}$ M uranium in the form of an aqueous uranyl nitrate solution, and 1-ml lots of $8.5 \cdot 10^{-4}$ M aqueous arsenazo solution, were introduced into a series of 25-ml standard flasks; 2 ml of a 0.5 N solution of an acetate buffer mixture was then added to each flask to establish the requisite pH. Fluorine was added to the solutions in the flasks in the form of sodium fluoride solution. All the solutions were made up to the mark with water and carefully mixed; after standing for 15-20 min their optical density was measured at 620 mμ in a 10-mm cuvette. The sensitivity of the determination depends on the conditions under which the reaction is carried out (Fig. 3). Accordingly, by varying them it is possible to determine fluoride over a wide concentration range: from hundredths of a microgram to milligrams per ml.

The optical density of solutions of the complexes of zirconium, thorium, and aluminum with arsenazo was determined in the same way on adding varying amounts of fluoride.

Table 1 contains the conditions for fluoride determination and the sensitivity of the method on using arsenazo with various metals (cuvette with a transmission layer of 10 mm). Optical density was measured on an SF-4 spectrophotometer. From the results given in Figs. 1-3 and in Table 1, it is clear that the effect of fluoride ions decreases with increasing pH. This is explained by the fact that the reagent arsenazo is a sexibasic acid, the last four dissociation stages of which characterize arsenazo as a weak acid [8].

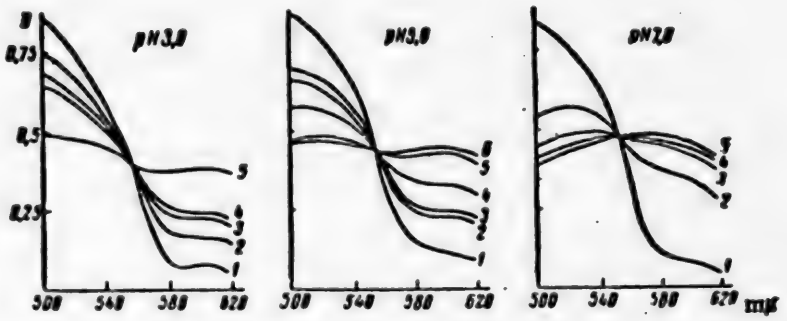

Fig. 1. Changes in the absorption spectra of solutions of the uranyl-arsenazo complex on adding sodium fluoride. Uranium concentration $2 \cdot 10^{-5}$ M; arsenazo concentration $3.4 \cdot 10^{-5}$ M. Series of curves at pH 3.0: 1) fluoride concentration $1 \cdot 10^{-3}$ M; 2) $4 \cdot 10^{-4}$ M; 3) $2 \cdot 10^{-4}$; 4) 10^{-4}; 5) 0.0. Series of curves at pH 5.0: 1) fluoride concentration $1 \cdot 10^{-2}$ M; 2) $6 \cdot 10^{-3}$; 3) $4 \cdot 10^{-3}$; 4) $2 \cdot 10^{-3}$; 5) $1 \cdot 10^{-3}$; 6) 0.0. Series of curves at pH 7.5: 1) fluoride concentration $3.5 \cdot 10^{-1}$; 2) $2 \cdot 10^{-1}$; 3) $1 \cdot 10^{-1}$; 4) 0.0; 5) $5 \cdot 10^{-1}$.

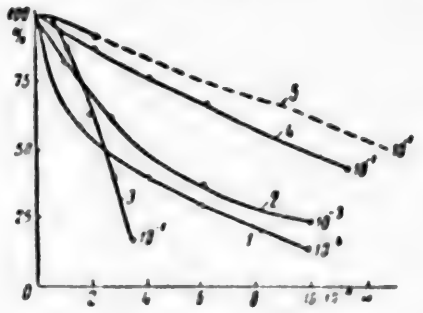

Fig. 2. Change in the concentration of the uranyl-arsenazo complex on adding fluoride. Uranium concentration $2 \cdot 10^{-5}$ M, arsenazo concentration $3.4 \cdot 10^{-5}$ M. 1) pH 3.0; 2) pH 5.0; 3) pH 7.5; 4) pH 9.0; 5) pH 10.0.

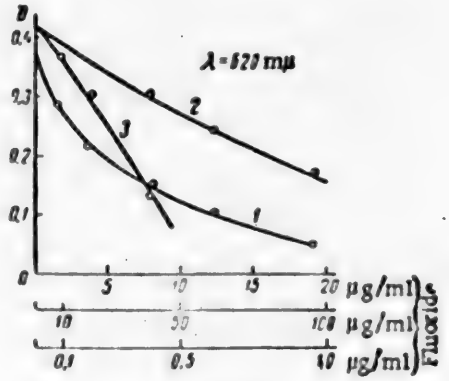

Fig. 3. Calibration curve for fluoride determination on the basis of the decrease in the color intensity of the uranyl-arsenazo complex. Uranium concentration $2.0 \cdot 10^{-5}$ M; reagent concentration $3.4 \cdot 10^{-5}$M. 1) pH 3.0; 2) 5.0; 3) 7.0.

As shown earlier [9], metal ions replace the hydrogen ions in the arseno group or in the hydroxy group of the arseno molecule, splitting of hydrogen from which is exactly characterized by low values of the dissociation constants. Accordingly, on increasing the pH the concentration of the coordinated anions of the reagent increases, and consequently the resistance to the destructive action of fluoride ions on the color increases. On the other hand, on lowering the pH the destructive effect of fluoride on the color increases, and in certain cases can give rise to conditions such that the effective stability of the fluoride complex will be higher than the effective stability of the colored complex (e.g., in the system aluminum-arsenazo-fluoride at pH 3.5-4.5).

Under these conditions the fluoride is complexed with the metal into a complex in equivalent amounts; consequently, similar conditions can be used for the titrimetric determination of fluorine. The regularities indicated are confirmed experimentally by the results of the present work.

The results in Table 1 show that determination of fluoride on the basis of the extinction of the color of the arsenazo complex with aluminum is more sensitive than when other ions are used to form complexes with arsenazo; the color of the aluminum complex, however, depends to a greater extent on pH. The relatively high sensitivity of

TABLE 1. Conditions for the Interaction of Fluorine with Arsenazo Complexes

Concentrations: element C_1 and reagent C_2, M	pH	Fluoride concentration range examined, M	Measurement wave length D, mμ	Fluoride concentration D_0 decreasing to ½ value	Sensitivity of determination (1.0-cm cuvette) mg/ml	Working rate of fluoride concentration (25 ml)
Aluminum						
$C_1 = 5{,}3 \cdot 10^{-5}$	3,0	$0—1{,}9 \cdot 10^{-4}$	580	$5{,}4 \cdot 10^{-5}$	0,000068	2—50 μg
$C_2 = 6{,}8 \cdot 10^{-5}$	5,0	$0—2{,}9 \cdot 10^{-4}$	580	$6{,}5 \cdot 10^{-5}$	0,00003	2—50 μg
	7,5	$2{,}9 \cdot 10^{-3}—2 \cdot 10^{-2}$	580	$1{,}2 \cdot 10^{-2}$	0,12	Spectra not very clear
$C_1 = 4 \cdot 10^{-5}$	4,5	$0—8{,}3 \cdot 10^{-5}$	575	$3{,}4 \cdot 10^{-5}$	0,000026	2—40 μg
$C_2 = 8 \cdot 10^{-5}$						
$C_1 = 8 \cdot 10^{-5}$	4,5	$0—1{,}7 \cdot 10^{-4}$	575	$7{,}6 \cdot 10^{-5}$	0,000037	2—70 μg
$C_2 = 8 \cdot 10^{-5}$						
Thorium	1,5	$0—1{,}2 \cdot 10^{-4}$	600	$1{,}3 \cdot 10^{-4}$	0,00007	5—100 μg
$C_1 = 4 \cdot 10^{-5}$	2,05	$0—1{,}2 \cdot 10^{-4}$	600	$2{,}3 \cdot 10^{-4}$	0,00014	0,01—0,2 mg
$C_2 = 6 \cdot 10^{-5}$	2,95	$0—1{,}2 \cdot 10^{-4}$	600	$2{,}7 \cdot 10^{-4}$	0,00014	0,01—0,2 mg
	2,7	$0—2{,}1 \cdot 10^{-3}$	600	$8{,}7 \cdot 10^{-4}$	0,0065	0,01—1 mg
	5,3	$0—3{,}1 \cdot 10^{-3}$	600	$1{,}3 \cdot 10^{-3}$	0,0073	0,02—1,5 mg
	5,8	$0—4{,}2 \cdot 10^{-3}$	600	$2{,}3 \cdot 10^{-3}$	0,0013	0,035—2,0 mg
	7,0	$0—2{,}1 \cdot 10^{-2}$	600	$6{,}7 \cdot 10^{-3}$	0,0059	0,15—10 mg
	9,0	$0—2{,}1 \cdot 10^{-1}$	600	$1{,}1 \cdot 10^{-1}$	0,080	2,0—50 mg
	10,5	Spectra not very clear				
Zirconium	1,0	$0—2{,}4 \cdot 10^{-4}$	620	$7 \cdot 10^{-5}$	0,00032	8—50 μg
$C_1 = 4 \cdot 10$						
$C_2 = 3{,}4 \cdot 1$	3,0	$0{,}1 \cdot 10^{-3}$	620	$3{,}5 \cdot 10^{-4}$	0,0024	0,060—0,5 mg
	5,0	$0—8 \cdot 10^{-3}$	620	$6 \cdot 10^{-4}$	0,0019	0,05—0,5 mg
	7,5	$0—1 \cdot 10^{-1}$	620	$1 \cdot 10^{-1}$	0,95	Spectra not very clear
Uranyl						
$C_1 = 3{,}4 \cdot 10^{-5}$	3,0	$0—9{,}6 \cdot 10^{-4}$	620	$2{,}5 \cdot 10^{-4}$	0,0068	0,015—0,45 mg
$C_2 = 6{,}8 \cdot 10^{-5}$	5,0	$0—9{,}6 \cdot 10^{-3}$	620	$4 \cdot 10^{-3}$	0,0057	0,14—5 mg
	7,5	$0—3{,}4 \cdot 10^{-1}$	620	$2{,}5 \cdot 10^{-1}$	0,19	0,5—100 mg
	9,0	$0—5{,}7 \cdot 10^{-1}$	620	1,1	0,72	14,5—500 mg
	10,5	Spectra not very clear				

TABLE 2. Stability of the Complex Compounds of Arsenazo and Fluoride

Element	Instability constants of the complexes		Ratio of instability constants $K_a : K_F$
	with arsenazo	with fluoride	
Aluminum	$1{,}5 \cdot 10^{-10}$	$4{,}8 \cdot 10^{-7}$	$3 \cdot 10^{-4}$
Beryllium	$2{,}2 \cdot 10^{-9}$	$1{,}4 \cdot 10^{-6}$	$1{,}57 \cdot 10^{-3}$
Gallium	$1{,}7 \cdot 10^{-10}$	—	—
Iron	$3{,}9 \cdot 10^{-14}$	$1{,}9 \cdot 10^{-6}$	$2 \cdot 10^{-8}$
Indium	$1{,}9 \cdot 10^{-11}$	—	—
Rare earths	$1{,}0 \cdot 10^{-10}$	$1 \cdot 10^{-4}$	$1 \cdot 10^{-6}$
Thorium	$1{,}6 \cdot 10^{-10}$	$1{,}6 \cdot 10^{-5}$	$1 \cdot 10^{-5}$
Titanium	$5{,}8 \cdot 10^{-18}$	$1 \cdot 10^{-7}$	$6{,}0 \cdot 10^{-10}$
Uranium (IV)	$6{,}0 \cdot 10^{-17}$	10^{-7}	$6 \cdot 10^{-10}$
Uranyl ion	$2{,}5 \cdot 10^{-13}$	10^{-8}	$2{,}5 \cdot 10^{-6}$
Zirconium	$1{,}9 \cdot 10^{-17}$	$1{,}15 \cdot 10^{-9}$	$1{,}65 \cdot 10^{-8}$

fluoride determination with aluminum is related to the lower stability of the complex formed between aluminum and arsenazo compared with the stabilities of the remaining complexes. A buffer solution must be used to standardize the experimental conditions and the reproducibility of the results. The amount of buffer solution added should be constant in all series of experiments, since the acetate ion which enters into its composition also forms a fairly stable complex with aluminum cations and uranyl ions.

Table 2 contains some properties of the complex compounds of arsenazo and fluoride, which make it possible

to evaluate the possibility of using colored compounds of arsenazo for determining fluoride. The K_{instab} values of the complexes of arsenazo were determined spectrophotometrically by comparison with the stability of the colorless complexes of the metals (fluorides, oxalates, etc.) studied. Details of the experimental method used are given in [9]. The highest sensitivity, using the same conditions for carrying out the reaction, will be observed in those cases where the difference in the value of the instability constants of the arsenazo complexes on the one hand, and the fluoride complexes on the other, will be least, e.g., in the case of aluminum or beryllium.

Determination of fluoride with thorium and the uranyl ion will be somewhat less sensitive, and even less sensitive with zirconium and titanium. Reactions with titanium and zirconium are insuitable also, since the absorption spectra of solutions of their compounds with arsenazo are close to the spectra of the reagent and the molar extinction coefficient of solutions of the complexes are comparatively low, while the composition of the complexes changes with pH. In addition, the reactions of zirconium and quadrivalent titanium are unbalanced; the ions hydrolyze, as a result of which nonreproducible results are obtained. This last fact shoud be borne in mind in other methods where colored titanium and zirconium complexes are used.

SUMMARY

Colored complexes of the reagent arsenazo have been used for the determination of fluoride ions. The most suitable compounds for this purpose are those of aluminum, the uranyl ion, beryllium, thorium, and the rare earths.

Conditions are given for the determination of fluoride ions over a wide concentration range (from hundredths of a microgram to tenths of a milligram per ml) on the basis of the decrease in color intensity.

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SEPARATE POTENTIOMETRIC TITRATION OF MIXTURES OF ORGANIC BASES IN A METHYL ETHYL KETONE MEDIUM WITH PERCHLORIC ACID SOLUTION

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Numerous investigations in the field of solutions carried out by the Russian school of chemists under D. I. Mendeleev [1-3] have exposed the extremely important fact of the influence of the individual character of a solvent on the state of the dissolved material in solution.

It has been found that the same material, e.g., urea [4], can behave in various ways depending on the nature of the solvent. It is possible to titrate in nonaqueous solvents weak and very weak acids and bases which cannot be titrated in aqueous media because of high pK_{base} values.

Anhydrous acetic acid is the medium that is most frequently used for titrating bases [5-8]. It is possible to titrate such bases as amines, alkaloids, and antibiotics, etc., in acetic acid with reasonable accuracy [9]. As a titration medium, however, acetic acid has several disadvantages [10].

All strongly protogenic solvents have a leveling effect on base strength, so that it is impossible to determine bases separately in their mixtures. Recently, in some instances, formic acid [11], a mixture of acetic and formic acids [12], acetic acid and its anhydride [13], butyric acid [14], propionic acid [15], and other acids have started to find application for titrating weak bases instead of acetic acid.

Theoretical considerations relating to the use of protogenic solvents of the acetic acid type as titration media have been considered by Izmailov [16].

Fritz [17] has used acetonitrile as a medium for titration mixtures of bases. Since solutions of perchloric acid in acetonitrile are unstable, titration was carried out with a solution of perchloric acid in dioxane. The author succeeded in carrying out separate determination of di-n-butylamine and pyridine, aniline and o-chloroaniline, β-phenylethylamine and aniline, pyridine and caffeine, aniline and sulfothiazole. It is also possible to titrate mixtures of Schiff bases and the original amine in an acetonitrile medium [18].

Dalit has carried out separate titrations of diethylamine and pyridine in their mixtures in a propylene glycol–chloroform medium. Nevertheless, on titrating a mixture of diethylamine and aniline in the same solvent only one potential jump corresponding to the total of both bases was obtained. It has been found possible to carry out potentiometric titration of the following two-component mixtures in an ethylene glycol–phenol medium (1:1): triethylamine and aniline, triethylamine and pyridine, and ammonia and an aqueous solution of pyridine [10].

Pifer, Wollish, and Schmall [19] have titrated mixtures of potassium and ammonium acetates with n-butylamine or pyridine in an acetic acid–chloroform (1:10) medium.

Bruss and Wyld [20] have titrated acid mixtures and also piperidine and pyridine in a methyl isobutyl ketone medium.

We have tested protogenic solvents (acetic, formic, and propionic acids), amphoteric solvents, and a series of inert solvents as media for titrating mixtures of organic bases. The use of solvents which do not exert a levelling effect on bases makes it possible to carry out separate titration of bases in their mixtures.

Ketones proved to be the best differentiating solvents. These solvents possess both weakly acid and weakly basic properties simultaneously. Of the ketones tested, including acetone, methyl ethyl ketone, methyl butyl ketone, acetophenone, and others, methyl ethyl ketone proved to be the best. In this medium it is possible to carry out

separate titration of multicomponent mixtures of strong, weak, and very weak acids [21].

On the basis of the research work indicated above, we have developed a new method for the determination of weak and very weak bases in their mixtures by titration in a methyl ethyl ketone medium, using perchloric acid dissolved in the same solvent as titrant. The method suggested has many advantages over titration of bases in an anhydrous acetic acid medium.

Taking neutralization of pyridine as an example, the neutralization of a base can be expressed in the form of the following equations:

$$CH_3COCH_2CH_3 \rightleftarrows CH_3-\overset{OH}{\overset{|}{C}}-CH_2CH_3$$

$$C_5H_5N+CH_3-\overset{OH}{\overset{|}{C}}-CH_2CH_3 \rightleftarrows C_5H_5NH^+ + CH_3-\overset{O^-}{\overset{|}{C}}-CH_2CH_3$$

$$HClO_4+CH_3COCH_2CH_3 \rightleftarrows CH_3COCH_2CH_3+ClO_4^-$$

$$CH_3\overset{H^+}{C}OCH_2CH_3+CH_3-\overset{O^-}{\overset{|}{C}}-CH_2CH_3 \rightarrow 2CH_3COCH_2CH_3$$

$$C_5H_5NH^+ + ClO_4^- \rightleftarrows C_5H_5NH^+ClO_4^-$$

According to Izmailov [5], the change in titration conditions which occurs in nonaqueous solvent medium is explained by the change in the ratio K_S/K_B, where K_S is the ionic product of the solvent, and K_B is the dissociation constant of the base. A decrease in this ratio leads to improvement in titration conditions. Thus for formic acid, which has strong acid properties, $K_S = 5 \cdot 10^{-7}$, while for a weak base such as urea, $K_B = 5.6 \cdot 10^{-2}$, while in water K_B for urea is $1.5 \cdot 10^{-14}$. In an aqueous medium the ratio $\frac{K_S}{K_B} = \frac{1 \cdot 10^{-14}}{1.5 \cdot 10^{-14}} \approx 1$, while in a formic acid medium $\frac{K_S}{K_B} = \frac{5 \cdot 10^{-7}}{5.6 \cdot 10^{-2}} \approx 10^{-5}$. Accordingly, in a formic acid medium, just as in a medium of other acid solvents [22], weak bases become stronger and can be titrated with reasonable accuracy.

In an acetone medium, which possesses weakly acid properties, the ratio K_S/K_B decreases insignificantly, but the ratio is still sufficient for weak bases such as aniline and its derivatives to be titrated in a medium of actone and other ketones.

EXPERIMENTAL

We have titrated aliphatic and aromatic primary, secondary, and tertiary amines (e.g., n-butylamine, triethylamine, triethanolamine, aniline, dimethylaniline, diethylaniline, toluidines, etc.), heterocyclic bases (pyridine, piperidine, pyrazoles, triazoles, imidazoles etc.) in methyl ethyl ketone. Methyl ethyl ketone was carefully dehydrated by standing for a long time over anhydrous potassium carbonate. Before use it was distilled and the fraction boiling between 79-80° collected. Solutions of perchloric acid in acetic acid, dioxane, acetone, and methyl ethyl ketone were tested as titrants.

A 0.1 N solution of perchloric acid in methyl ethyl ketone is recommended for the separate determination of the components of mixtures of bases. Such a standard solution is prepared by dissolving 8-9 ml of 72% perchloric acid in 1000 ml of dried methyl ethyl ketone; the solution is saturated with dry nitrogen for 5 min. The solution is standardized either against potassium hydrogen phthalate or sodium carbonate [9]. The titer of a solution of perchloric acid in methyl ethyl ketone remains constant for a month.

The use of a dioxane solution of perchloric acid did not give such good results as the use of a perchloric acid solution prepared in methyl ethyl ketone.

Experimental Procedure. The setup consists of a 10-ml buret graduated in 0.02 ml, an LP-5 potentiometer, a magnetic stirrer, a nitrogen drying system, and a titration beaker in which glass and calomel electrodes are immersed.

An accurately weighed sample of test material (0.03-0.05 g) is transferred to the titration beaker and dissolved in 20 ml of methyl ethyl ketone.

Ten ml of the 0.1 N solution of perchloric acid in methyl ethyl ketone is squeezed into the buret by means of a rubber bulb. In order to purify and dry the air squeezed into the buret, a system of columns packed with soda lime and fused calcium chloride is inserted between the buret and the rubber bulb.

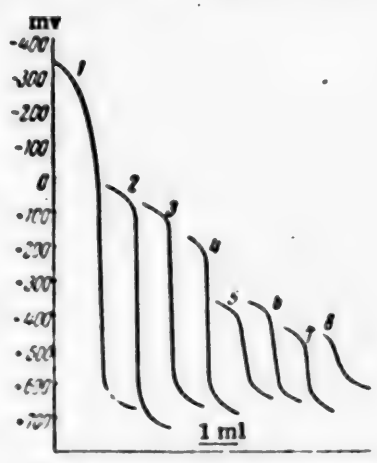

Fig. 1. Potentiometic titration curves for individual bases in a methyl ethyl ketone medium, the titrant being a solution of perchloric acid in the same solvent. 1) Tetraethylammonium hydroxide; 2) piperidine; 3) triethylamine; 4) o-phenanthroline; 5) benzimidazole; 6) tyramine; 7) acridine; 8) 3,5-dimethylpyrazole.

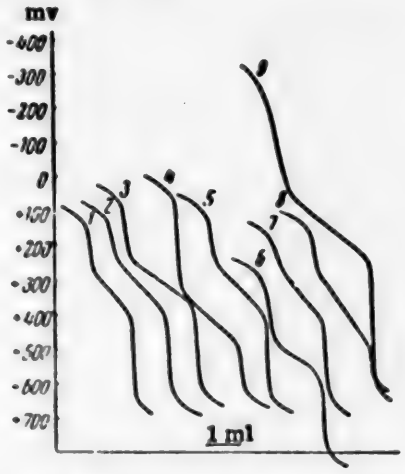

Fig. 2. Potentiometric titration curves of two-component mixtures in methyl ethyl ketone. 1) Triethylamine + o-phenanthroline; 2) triethylamine + benzimidazole; 3) piperidine + benzimidazole; 4) piperidine + 3,5-dimethylpyrazole; 5) potassium hydroxide + o-phenanthroline; 6) tyramine + acridine; 7) tyramine + o-phenanthroline; 8) tyramine + 3,5-dimethylpyrazole; 9) tetraethylammonium hydroxide + tyramine.

Titration is carried out potentiometrically, using a glass electrode and a modified calomel electrode in a stream of dry nitrogen, which is passed into the titration beaker to prevent absorption of carbon dioxide and moisture from the air.

The titrant is added in 0.1-ml portions until the equivalent potential is established, after which it is added in 0.05-ml portions. Titration is continued until a constant potential is established.

The test bases possess different strengths in a methyl ethyl ketone medium (Fig. 1). The strongest base proved to be tetraethylammonium hydroxide, whose potential jump during titration was 700 mv (Curve 1). Piperidine and triethylamine (Curves 2 and 3 respectively) are weaker bases, their strengths being approximately equal. o-Phenanthroline proved to be even weaker (Curve 4). Benzimidazole (Curve 5) and tyramine (Curve 6) have approximately equal strengths in methyl ethyl ketone. The weakest bases are acridine (Curve 7) and 3,5-dimethylpyrazole (Curve 8).

Comparison of the titration curves of individual bases with titration curves of their mixtures showed that two bases can be titrated separately in their mixtures if the difference between the beginning of their potential jumps during titration of the individual bases is about 100 mv. Thus, the difference between the beginning of the jumps during titration of triethylamine (Fig. 1, Curve 3) and o-phenanthroline (Fig. 4, Curve 4) amounts to 100 mv.

The result of titrating a mixture of triethylamine and o-phenanthroline is shown in Fig. 2. The curve has two distinct potential jumps, the first corresponding to completion of the neutralization of triethylamine and the second to neutralization of o-phenanthroline.

Curve 2 (Fig. 2), which is the titration curve for a mixture of triethylamine and benzimidazole, also has two potential jumps. The difference between the beginning of the potential jumps of these bases (Fig. 1) is 300 mv.

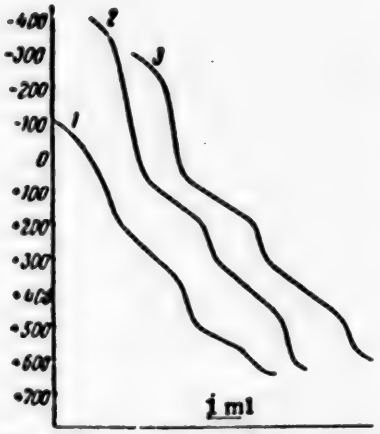

Fig. 3. Potentiometric titration curves for three-component mixtures in methyl ethyl ketone. 1) Potassium hydroxide + benzimidazole + p-aminoazobenzene; 2) tetraethylammonium hydroxide + tyramine + acridine; 3) tetraethylammonium hydroxide + tyramine + 3,5-dimethylpyrazole.

During titration of a mixture of piperidine and benzimidazole (Curve 3) a curve with two potential jumps is obtained, the jumps corresponding to completion of separate neutralization of piperidine and benzimidazole. The remaining curves in Fig. 2 are also curves for titration of two-component mixtures: Curve 4 for a mixture of piperidine and 3,5-dimethylpyrazole, Curve 5 for potassium hydroxide and o-phenanthroline, Curve 6 for tyramine and acridine, Curve 7 for tyramine and o-phenanthroline, and Curve 8 for tyramine and 3,5-dimethylpyrazole. Two potential jumps are clearly observed on all the curves, the jumps corresponding to completion of the separate neutralization of the components of the mixture.

Fig. 3 shows the titration curve obtained on titrating a three-component mixture of bases. Curve 1 was obtained on titrating a mixture of potassium hydroxide, benzimidazole, and p-aminoazobenzene. The three distinct potential jumps show that each component of the mixture was titrated separately.

A curve with three potential jumps was obtained on titrating a mixture of tetraethylammonium hydroxide, tyramine, and acridine (Curve 2). The first jump corresponds to complete neutralization of tetraethylammonium hydroxide as the strongest base, the second to neutralization of tyramine, and the third to neutralization of acridine. Curve 3 was obtained on titrating a mixture of tetraethylammonium hydroxide, tyramine, and 3,5-dimethylpyrazole. The three components are again titrated separately even in this case. The first potential jump corresponds to complete neutralization of tetraethylammonium hydroxide, the second to tyramine, and the third to 3,5-dimethylpyrazole.

Table 1 contains the results obtained during quantitative determination of some organic bases by titration in a methyl ethyl ketone medium with a methyl ethyl ketone solution of perchloric acid. Individual bases can be determine by this method to an accuracy of 1%.

TABLE 1. Determination of Individual Bases by Titration in a Methyl Ethyl Ketone Medium

Test material	Sample wt., g	Found, g	Error, rel. %
3,5-Dimethylpyrazole	0,0800	0,0809	+1,0
o-Phenanthrolin	0,0552	0,0557	+0,9
Tyramine base	0,0328	0,0328	0,0
Tetraethylammonium hydroxide	0,0814	0,0818	+0,4
Acridine	0,0460	0,0456	−0,9

The suitability of the suggested method for quantitative analysis of two- and three-component mixtures of bases is demonstrated in Table 2. The components of the mixtures can be determined to an accuracy of 1 to 3%.

SUMMARY

A new potentiometric method has been developed for the separate determination of bases in their mixtures; it is based on titration in a methyl ethyl ketone medium using a solution of perchloric acid in the same solvent as titrant. Methyl ethyl ketone has the advantage over acetic acid as a solvent for test materials and as a titrating medium that it is possible to carry out separate titration of multicomponent mixtures of bases in it.

TABLE 2. Analysis of Two- and Three-Component Mixtures of Bases

Components	Sample wt., g	Found, g	Error, rel. %
Tyramine Acridine	0,0471 0,0783	0,0463 0,0798	−1,7 +1,8
Tyramine 3,5-Dimethylpyrazole	0,0428 0,0526	0,0426 0,0574	−0,4 +2,0
Tyramine o-Phenanthroline	0,0334 0,0473	0,0328 0,0448	+1,8 +3,0
Tetraethylammonium hydroxide Tyramine	0,0484 0,0356	0,0485 0,0364	+0,2 +1,9
Tetraethylammonium hydroxide Tyramine Acridine	0,0484 0,0282 0,0642	0,0487 0,0256 0,0625	+0,6 −2,1 −2,8
Tetraethylammonium hydroxide Tyramine 3,5-Dimethylpyrazole	0,0484 0,0356 0,0375	0,0485 0,0364 0,0384	+0,2 +1,9 +0,5

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MICROANALYTICAL HYDROGENATION

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Warburg's manometric method [1,2] permits determination of the amount of gas formed or used up in a system at constant temperature and volume, on the basis of changes in gas pressure. This method ensures a high experimental accuracy in gas microanalysis as compared with the volumetric method (measurement of changes in volume at constant pressure), since small changes in the volume of a gas in a system can be observed more readily by means of a manometric method than by direct change in volume. Thus Schwabe [3] has pointed out that the use of Warburg's technique permits changes in volume of a gas to be measured with an accuracy of ± 0.003 cm^3.

There are published references to the use of a manometric method of microanalytical hydrogenation. Kuhn and Moller [4] have developed a differential-manometric method of microhydrogenation, based on measurements of the difference in two vessels in which the test and a standard are hydrogenated under identical conditions. This method, which ensures and accuracy of measurement of ± 0.5% during a 40 hour hydrogenation using a 5-mg aliquot of test material, is rather difficult and complicated. Umbreit et al. ([1], p. 141) have developed a simple manometric method using standard Warburg apparatus for the analytical hydrogenation of pyridoxal, the accuracy being ± 4%.

The present article is devoted to the development of a simple manometric method for microanalytical hydrogenation using a Warburg apparatus. We have succeeded in designing special hydrogenation cells and have developed a technique for catalytic heterogeneous hydrogenation, which makes it possible to carry out microanalytical determinations and to study the kinetics of the process indicated.

EXPERIMENTAL PART AND DISCUSSION OF RESULTS

a) Preparation of Purification of Hydrogen. The hydrogen used for hydrogenation was prepared electrolytically in an electrolyzer with Bruns's nickel electrodes [5]. The electrolyte was a solution of 200.0 g KOH and 50.0 g $Ba(OH)_2$ in 500 ml of water. The hydrogen formed after a preliminary drying over $CaCl_2$ was freed from traces of oxygen in a tube packed with palladinized asbestos heated at 300-350°, and from traces of H_2S in a wash bottle containing 20% NaOH solution saturated with PbO. The gas was next freed from splashes of alkali solution in a splash head and in a tube filled with glass wool, and finally in a $CaCl_2$ tube.

b) Modification of Warburg Apparatus for Hydrogenation. We used Warburg apparatus produced by the "Labor" firm (Hungary) for studying cell respiration. This apparatus consists of a water thermostat with a turbine stirrer and a mercury-toluene thermoregulator which ensures that the temperature in the bath can be kept to an accuracy of ± 0.05° over the range 20-80°. Oscillating panels with a maximum number of oscillations of 260 per min are fitted to the side walls of the thermostat. The amplitude and oscillating rate are readily regulated. Warburg manometers, connected via ground joints to vessels which are immersed in the water thermostat, are fitted by means of special clips to the panels.

In the course of our work we became convinced, despite Umbreit's ([1], p 141) directions regarding the use of a standard system of Warburg respirometers for microanalytical hydrogenation, that they suffer from the following disadvantages which hinder their use: 1) because of the low depth of the retort, the material being hydrogenated is thrown out prematurely into the working space of the vessel during saturation of the catalyst with hydrogen; 2) during oscillation (shaking), the catalyst collects on the bottom of the vessel and is thereby withdrawn from the reaction; 3) grease from the ground joint falls into the hydrogenzation vessel; 4) it is very difficult to replace the air completely by hydrogen even when the hydrogen is passed for a long time through the manometer into the Warburg vessel; 5) it is impossible to control the extent to which the catalyst is saturated with hydrogen during an experiment.

Taking all these drawbacks into account, we have modified the standard Warburg apparatus and adapted it for

Fig. 1. Hydrogenation vessel. 1) Horizontal section; 2) vertical tube; 3) ground joint; 4) side tube with ground joint; 5) rotating retort; 6) channel.

hydrogenation (Fig. 1). The working space of the vessel we used is a horizontal semicylinder with a flat bottom 1, the axis of the cylinder lying along the direction of oscillation. To the cylinder is connected a vertical tube 2 ending in an external ground joint 3 which prevents any grease getting into the vessel. A tube 4 is fused into the vertical part of the vessel at an angle of 60°; to this tube is connected a deep retort 5 which also has a ground joint and can be rotated. The ground joint of the retort is provided with a channel 6 which prevents any grease from passing inside the hydrogenation vessel.

The joints are lubricated with vacuum grease obtained by melting vaseline, paraffin, and natural rubber in the proportions 5 : 2 : 5. The design of the manometer was also modified to some extent (Fig. 2). To the rubber tube 2 was connected a two-way tap 3, connected by a rubber hose with the glass reservoir 5. This construction made it possible to evacuate the manometric liquid (mercury) from the manometer, and after covering the tap 3 to suck out the gas from the system by means of a water pump, and then fill the system with hydrogen through the three-way tap 6. Five successive evacuations and fillings of the system with hydrogen made it possible to remove the air completely from the system and to ensure a hydrogen atmosphere. Tap 3 was then closed, the reservoir plus rubber tube disconnected, and the apparatus placed in its original position. This was done by turning the screw clip while the manometer was fitted onto the Warburg vessel, and with the three-way tap open the level of the manometric liquid in both arms of the manometer was adjusted to the null point (a mark at 250 mm). The three-way tap was then closed, an experiment carried out, and the pressure change in the system measured from the change in the level of the manometric liquid in the left arm after the system had been adjusted to constant volume–setting the level of the manometric liquid at the null point in the right arm. The manometer readings were corrected by a so-called thermobarometer–the usual type of manometer with a Warburg vessel filled with the solvent used in the reaction, and operating under the same conditions as those in the working manometer. The latter makes it possible to take into account the effect of temperature changes in the bath and the surrounding air, and also of atmospheric pressure, on the change in gas pressure in the system during an experiment.

c) Measurement of the Volume of the Hydrogenation Vessel. The volume of the hydrogenation vessel and of that part of the manometer up to the null point was determined by a method described by Umbreit ([1], p. 85); this consists in weighing the mercury required to fill the space indicated.

d) Calculation of the Amount of Hydrogen Absorbed. The hydrogen used is calculated by means of the formula given in [1], p. 13:

$$x = \left[\frac{(V - V_1)\frac{273}{T} + V_1\alpha}{P_0}\right]h = Kh, \qquad (I)$$

where V is the volume of the hydrogenation vessel and the working part of the manometer, ml; V_1 is the volume of liquid in the vessel, ml; α is the solubility of hydrogen in the liquid, mg/ml at normal pressure; T is the experimental temperature in degrees absolute (273 + t°); P_0 is normal pressure (mm of the manometric liquid); h is the decrease in pressure in the system during an experiment (mm of manometric liquid); x is the amount of hydrogen used, ml; K is the vessel constant. Since $P_0 = \frac{760 \cdot 13.60}{d}$, where 760 is normal pressure in mm Hg, 13.60 is the sp. gr. of mercury, and d is the specific gravity of the manometric liquid, on the basis of equation I it is possible to write:

$$K = \frac{x}{h} = \frac{\left[(V - V_1)\frac{273}{T} + V_1\alpha\right]d}{760 \cdot 13.60} \qquad (II)$$

and, where mercury is the manometric liquid

$$K = \frac{(V - V_1)\frac{273}{T} + V_1\alpha}{760}. \qquad \text{(III)}$$

Since all the values which enter into formula II are constant for a given experiment, determination of the gas used reduces to multiplying the value of the vessel constant K by the change in the level of the manometric liquid h.

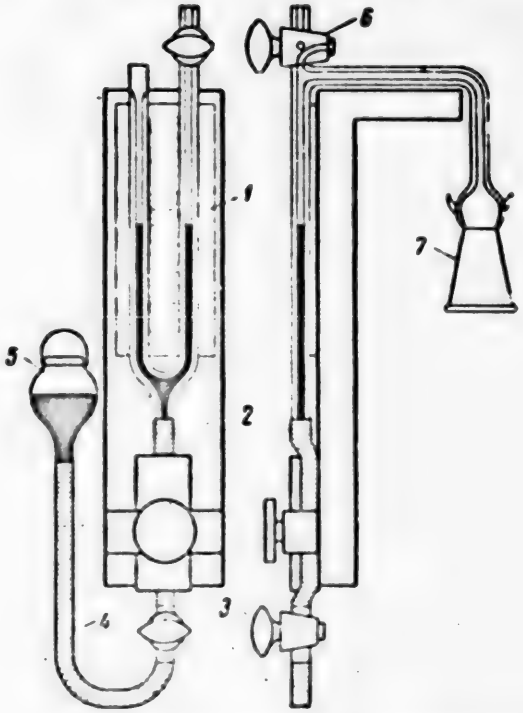

Fig. 2. Modified manometer. 1) U-shaped manometer tube; 2) rubber tube; 3) three-way tap; 4) rubber hose; 5) glass reservoir; 6) three-way tap; 7) outlet tube with ground joint for connecting to hydrogenation flask.

It also follows from formula II that the value of K characterizes the sensitivity of the hydrogenation apparatus. In order to increase the sensitivity of the apparatus the vessel constant K should be lowered. Of particular importance is the decrease in specific gravity of the manometric liquid, since a change of d from 13.60 (mercury) to 0.80 (96° ethanol) increases the sensitivity of the method 17 times without any need for altering the construction and geometrical parameters of the hydrogenation cell.

e) Hydrogenation of Maleic Acid over Palladium Oxide. The efficiency of the apparatus developed was checked by hydrogenating maleic acid which had been recrystallized three times from twice-distilled water. Palladium oxide was prepared by Adams's method [6]. A suspension of 0.7-1.6 mg of PdO in 1 ml of twice-distilled water was placed in the operating part of the hydrogenation vessel (see Fig. 1); a solution of 11.8-12.6 mg of maleic acid in 1.2 ml of twice-distilled water was introduced into the side retort. The system was filled with hydrogen and the catalyst saturated with hydrogen by shaking the flask 100-120 times per minute. After hydrogen had ceased to be absorbed by the palladium oxide, the level of the mercury in both arms of the manometer was adjusted to the null point, after which the retort containing the maleic acid solution was turned over and hydrogenation of the maleic acid carried out at the maximum shaking rate of 240-260 oscillations per minute, the path of the reaction being followed by observing the decrease of hydrogen pressure in the system. Completion of hydrogenation is assessed from cessation of hydrogen absorption. The experiments were carried out at 40 ± 0.05°.

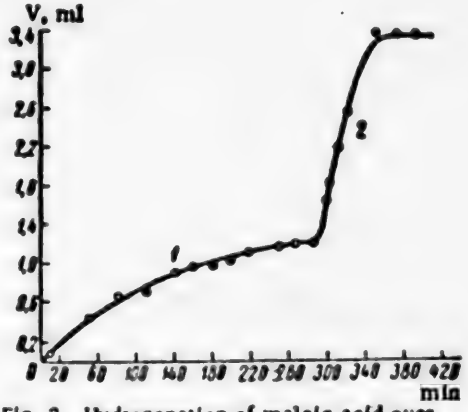

Fig. 3. Hydrogenation of maleic acid over PdO. 1) Saturation of catalyst with hydrogen; 2) hydrogenation of maleic acid.

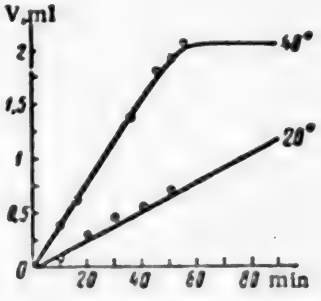

Fig. 5. Hyurogenation of maleic acid over a Pd-Cu catalyst.

Fig. 4. Hydrogenation vessel with fixed catalyst.

Results of one of these experiments are shown in Fig. 3; this curve shows the kinetic curves of the saturation of catalyst with hydrogen, and hydrogenation of maleic acid. Measurements showed that an increase in the amount of PdO favors an increase in reaction rate. Thus by altering the proportion by weight of PdO and maleic acid from 0.05 to 0.13 it is possible to cut down the hydrogenation time from 165 to 60 min.

Good reproducibility of results was observed in the experiments described; they did not differ from each other by more than 0.4%, while the deviation from the theoretical value of the hydrogenation equivalent was 0.4-0.8% when 2.21-2.26 ml of hydrogen was used up in a vessel with a volume of 25.34 ml.

f) Study of the Kinetics of Hydrogenation of Maleic Acid over a Copper-Palladium Catalyst. As is evident from Fig. 3, the kinetic curve of the hydrogenation of maleic acid over PdO is of the first order. This regularity could be both a reflection of the true character of the catalytic process, and a result of diffusion complications developing on the catalyst surface. Support for the latter hypothesis comes from published references [7-9] to the fact that hydrogenation of maleic acid over palladium contacts is of zero order. In order to check on the possibility of using the suggested method for studying the kinetics of hydrogenation, we tried to eliminate diffusion complications. For this purpose we increased the shaking rate from 270 to 400 oscillations per min (requisite modifications were made to the Warburg apparatus). This increase in shaking rate, however, led to the catalyst being thrown into the vertical part of the hydrogenation vessel, and to its withdrawal from the sphere of reaction; accordingly, we decided to fix the catalyst in the working part of the vessel. The catalyst was used in the form of black placed on a platinum disc or grid with an area of 1.7 cm^2 fused into the horizontal part of the hydrogenation flask (Fig. 4). Instead of PdO we use a palladium-copper alloy containing 30 atomic % of Cu recommended by Tverdovskii and Kaprova [9]. This catalyst posseses a high activity in the hydrogenation of ethylene and acetylene bonds and is less likely to be poisoned than pure Pd. The Pd-Cu alloy was prepared by elecrolytic deposition from a bath consisting of a mixture of the following solutions: I) 0.200 g $PdCl_2 \cdot 2H_2O$ and 0.250 g $NaNO_3$ in 10 ml H_2O; II) 0.14 g $CuSO_4 \cdot 5H_2O$ and 0.360 g $(NH_4)_2SO_4$ in 10 ml H_2O; III) 0.14 N H_2SO_4 in a ratio by volume of I : II : III = 5.9 : 4.1 : 30. The deposition time was varied from 3 to 10 min at a current density of 70 ma/cm^2. The precipitate of copper-palladium black was washed with water and subjected to cathodic purification for removing adsorbed ions at current of 70 ma/cm^2 in the course of 30 min in

0.1 N HCl or 0.05 N H_2SO_4. Maleic acid was hydrogenated at 20 and 40° (± 0.05°) by the technique described above. The kinetic curve of absorption of hydrogen by the Pd-Cu catalyst is similar to the curve shown in Fig. 3 for PdO. When the Pd-Cu catalyst is used, the amount of hydrogen required for saturating the catalyst is almost five times the amount required for hydrogenating the maleic acid. This latter fact indicates the need for careful control of the saturation of catalyst with hydrogen during microanalytical hydrogenation. As in the case of PdO, it was observed that the larger amount of hydrogen used for saturating the catalyst, i.e., the greater the amount of catalyst taken for an experiment, the more rapid is the hydrogenation process. Kinetic curves for the hydrogenation of maleic acid are shown in Fig. 5. Results with good reproducibility were again obtained in these experiments (± 0.1%, with a deviation from the theoretical value of the hydrogenation equivalent of +0.4% when 2.04-2.14 ml of hydrogen was used in a vessel with a volume of 27.7 ml).

As is evident from Fig. 5, the kinetic curves for hydrogenation of maleic acid over a Pd-Cu catalyst have a shape characteristic of a zero order reaction (a reaction which is independent of the velocity constant and concentration). The velocity constants of the reaction was calculated by means of the formula: $K = \Delta x / \Delta t$ and were found to be $K_1 = 0.014$ ml/min and $K_2 = 0.039$ ml/min at 20 and 40° respectively.

The results obtained enables one to calculate the activation energy $E_A = \frac{4.575\,\Delta \ln K}{\Delta T^{-1}} = 9250$ cal/mole, which lies within the limits 1000 to 10 000 cal/mole obtained by Kobozev [10] for hydrogenation of ethylene derivatives. This indicates that it is possible to use the microanalytical apparatus we have developed for studying the kinetics of the hydrogenation process.

SUMMARY

An improved apparatus for microanalytical hydrogenation (hydrogenation vessels and manometers) permits quantitative hydrogenation of materials with a hydrogenation equivalent of about 100 with a accuracy of ± 0.5%, using a 10-mg sample, and using mercury as the manometric liquid.

Taking maleic acid as an example, it has been shown that it is possible to apply the improved apparatus to study of the kinetics of the catalytic hydrogenation of maleic acid.

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THE DECOMPOSITION OF ORGANIC COMPOUNDS IN A RAPID STREAM OF OXYGEN UNDER THE CONDITIONS OF MICROELEMENTAL ANALYSIS

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It has been assumed that during rapid methods of analysis by combustion in a gas stream [1] the material is first of all subjected to pyrolytic decomposition in the quartz test tube inserted in the combustion tube. It has been considered [2] that there may occur in the decomposition zone firstly tarring and coking of the material with loss of hydrogen and formation of a difficultly volatile resin, and secondly, splitting with formation of active fragments.* In order to confirm experimentally that such processes do in fact occur, we carried out interrupted combustion of test materials (i.e., discontinuous combustion) The first time that the decomposition process was interrupted was when visible changes in the material were detected; at this stage either qualitative tests were carried out for aldehydes and unsaturated compounds in the residue, or the residue and the apparatus used for absorbing carbon dioxide and water were weighed. From one to three interruptions were made during each experiment.

As one might have expected, during combustion of hydrobarbons we were able to detect qualitatively formation of aldehydes and unsaturates at the very beginning of combustion; this confirmed our assumption of the development of active fragments during decomposition.

Determination of water and carbon dioxide at various stages of the process enabled us to assess the changes in the proportion between carbon and hydrogen both in the residue and in the decomposition products. We expected to find that these proportions would differ sharply from the proportions for the original compound. Nevertheless, experiments with hydrocarbons, acids, alcohols, and ethers showed that this is not so. Actually, in almost all cases, the proportions of carbon and hydrogen in the original material and in the products of incomplete decomposition and in the residue were very close to each other. The only exceptions were compounds which split off water at comparatively low temperatures, e.g., sugar, crystallohydrates, etc. A curious feature was the fact that even when the residue in the quartz test tube appeared to be completely resinified, the proportion of hydrogen and carbon remained almost the same. Accordingly, resinification which is observable visually only proceeds to a small extent, although it leads to coloration of the residue.

All these facts lead one to think that combustion appears to proceed in layer fashion, in which each portion of material passes into the gaseous state on heating, then burns up completely, breaking down beforehand to form active fragments. This may occur both with participation of oxygen (formation of aldehydes during combustion of hydrocarbons) and without participation of oxygen (formation of unsaturates). It should be pointed out that similar results were obtained on varying the size of the quartz test tube used for combustion, even in the case when the size of the test tube enabled the decomposition of the whole mass of sample to occur at once.

Thus the suggestion which we made previously that decomposition in the test tube (preliminary pyrolysis) is accompanied by resinification of test material and splitting off of hydrogen was not confirmed. Formation of active fragments was confirmed experimentally. Accordingly, combustion in a test tube does not resolve into pyrolysis and oxidation stages, but proceeds, as usual, in accordance with the theory of combustion.

* By active fragments we mean thermal decomposition products which are more reactive than the original test material, e.g., aldehydes, unsaturated free radicals, hydrogen, etc.

EXPERIMENTAL

Combustion was carried out in the usual apparatus [1]. The test material was decomposed in a quartz test tube 50-70 mm long and with an internal diameter of 6-7 mm by gradually moving the burner from the open end of the test tube to its closed end, i.e., counter to the oxygen stream (20-40 ml/min). Combustion products were trapped and weighed as usual.

TABLE 1

Test Material	Degree of pyrolysis	Color	Presence of aldehydes
Paraffin	Not subjected to decomposition	None	None
"	To a light-yellow color	Dense violet	Present
"	To a dark-yellow color	Violet	"
"	Combustion almost to completion	None	None
$C_{22}H_{38}$	Not subjected to decomposition	"	"
"	To a light-yellow color	Violet	Present
$C_6H_5(CH_3)_3CH_3$	Ditto	"	"
Naphthalene	"	None	None
Benzene	"	"	"

TABLE 2

Solution to which a solution of $SbCl_3$ in chloroform was added	Color with $SbCl_3$	Presence of unsaturates
Chloroform	None	Absent
Paraffin dissolved in chloroform	"	"
Cinammic aldehyde in chloroform	Brown	Present
Paraffin taken to a weak-yellow color and dissolved in chloroform*	Ditto	"
Paraffin taken to a yellow color and dissolved in chloroform*	"	"

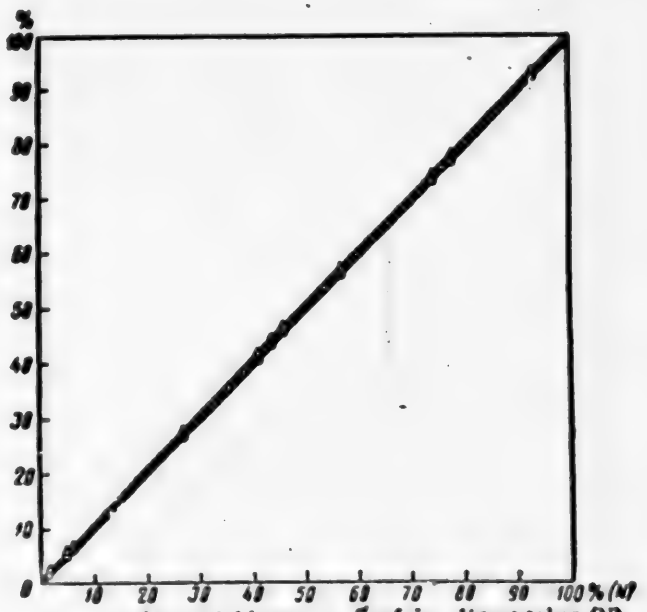
* Before addition of the antimony trichloride solution, the test samples only had a weak yellow color which did not change over a period of 6 hours.

The combustion was interrupted at various stages of decomposition. At the interruption the burner was removed and the combustion products expelled into the apparatus for absorbing water and carbon dioxide. After the interruption the residue of incompletely decomposed material in the test tube was tested for the presence of unsaturates and aldehydes in it, or the absorption apparatus was weighed; this was subsequently reconnected to the combustion tube, and combustion continued to completion or to the next interruption.

Qualitative Tests for Aldehydes. The residual material in the test tube used for decomposition was dissolved in chloroform and the solution transferred to a test tube. A freshly prepared solution of fuchsin sulfurous acid, which acquires a violet color in the presence of aldehydes, was added to the chloroform solution. From the results given in Table 1 it is clear that decomposition of aliphatic hydrocarbons is accompanied by formation of aldehydes.

Qualitative Tests for Unsaturates. The residual material in the test tube used for decomposition was dissolved in chloroform and the solution transferred to an ordinary test tube. To this solution was added a 30% solution of antimony trichloride in chloroform; in the presence of unsaturated compounds this solution turns brown. As the results in Table 2 show, decomposition of paraffin is accompanied by formation of unsaturates.

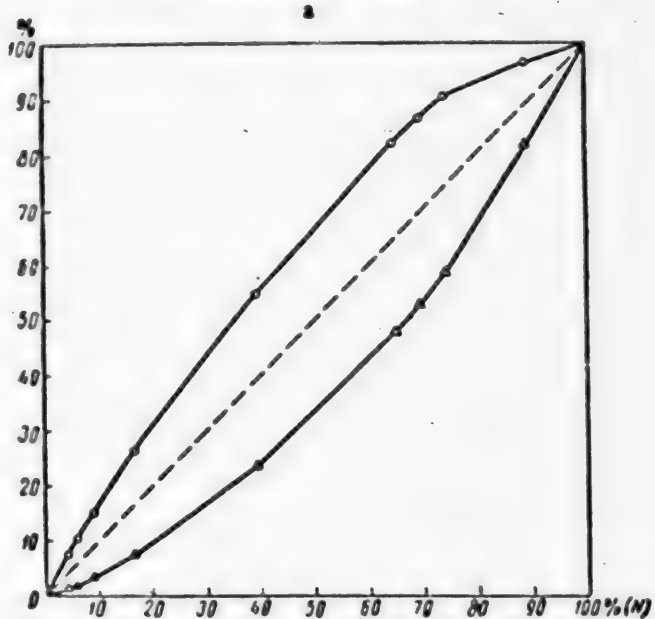
Determination of Carbon and Hydrogen at Various Stages of the Decomposition. On the basis of the results obtained on weighing the absorption apparatus after each interruption, the content of carbon and hydrogen in the burned-out part of the aliquot was calculated in relative percentages. Tables 3 and 4 contain some results of several combustions of various samples of each material. During combustion of one sample, 2-3 interruptions were made, as far as possible at different stages of decomposition. The tables indicate all the experiments carried out with a given test material, the results being arranged in order of increasing amount of the burned-out part of the sample of test material. The ratio of the percentage content of hydrogen to carbon indicates that the decomposition process occurs in layer fashion. Actually, it is only for materials which readily split off water that this ratio is greater than unity (Table 4); in all remaining cases it is almost equal to unity.



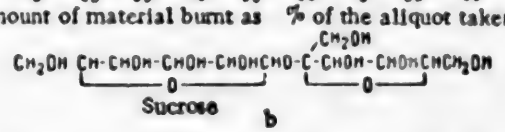
Amount of material burnt as % of the aliquot taken (N)

CH_3⟨⟩$C(CH_3)_2CH_2C_7H_{15}$

a



Amount of material burnt as % of the aliquot taken (N)



Sucrose

b

Curves for typical cases of burning of compounds during combustion with pyrolysis in the test tube used for decomposition. a) Test material which is not dehydrated on heating; b) material which is readily dehydrated on heating.

TABLE 3

Test substance	Amount, % C	Amount, % H	H/C	Test substance	Amount, % C	Amount, % H	H/C	Test substance	Amount, % C	Amount, % H	H/C
I	1,73	1,88	1,08	V	0,65	1,87	2,81	IX	18,12	19,48	1,07
	5,16	5,78	1,12		3,63	4,80	1,32		30,70	29,99	0,98
	6,18	6,26	1,01		10,88	14,83	1,36		73,03	75,94	1,04
	26,71	27,74	1,04		19,70	23,00	1,17		99,18	99,53	1,00
	40,75	41,91	1,02		30,23	31,09	1,05		100	100	1,00
	43,51	44,36	1,02		46,72	49,87	1,07				
	56,37	57,58	1,02		66,26	67,35	1,01				
	73,81	74,74	1,01		78,36	89,34	1,14				
	77,16	78,92	1,02		94,85	97,48	1,02				
	92,65	93,24	1,01		100	100	1,00				
	100	100	1,00								
II	0,76	1,30	1,71	VI	52,33	56,54	1,08	X	76,13	76,28	1,00
	17,00	18,04	1,01		61,15	64,72	1,06		89,98	89,77	0,99
	28,49	30,42	1,07		69,86	74,91	1,07		91,86	91,24	0,99
	43,60	46,34	1,06		100	100	1,00		100	100	1,00
	79,97	80,07	1,00								
	88,23	89,11	1,01								
	100	100	1,00								
III	0,90	1,66	1,84	VII	36,10	39,86	1,10	XI	9,75	11,68	1,20
	19,15	18,88	0,98		45,84	49,80	1,08		20,59	21,39	1,04
	25,49	24,66	0,96		54,06	57,63	1,07		47,92	49,77	1,03
	36,10	36,83	1,02		79,73	83,56	1,04		56,21	56,33	1,00
	44,03	44,11	1,00		100	100	1,00		82,40	82,62	1,00
	59,93	60,00	1,00						100	100	1,00
	88,81	90,94	1,02								
	100	100	1,00								
	28,88	30,93	1,07	VIII	2,78	5,77	2,08	XII	13,83	23,70	1,71
	37,47	40,07	1,04		31,68	31,96	1,00		31,80	37,83	1,19
	43,24	44,02	1,02		62,04	60,50	0,97		53,64	58,33	1,09
	59,12	57,83	0,96		99,61	97,54	0,98		74,60	78,09	1,04
	71,91	72,64	1,00		100	100	1,00		91,05	93,04	1,02
	95,24	95,60	1,00						100	100	1,00
	100	100	1,00								

I—$CH_3C_6H_4C(CH_3)_2CH_2C_6H_{13}$; $C_{18}H_{30}$

II—$C_6H_5C(CH_3)_2C(OH)(C_6H_{13})C_2H_5$; $C_{15}H_{24}O$

III—$CH_3C_6H_4C(CH_3)_2CH_2COOH$; $C_{12}H_{16}O_2$

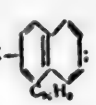
IV—$CH_3C_6H_4C(CH_3)_2CH_2C_4H_{10}$ (C=O); $C_{13}H_{18}O$

V—$C_{10}H_{21}COOH$; $C_{11}H_{22}O_2$

VI—$C_6H_5CH(C_2H_5)CH{-}CH_2$; $C_{10}H_{12}$

VII—$C_6H_5CH{-}CHCHO$; C_9H_8O

VIII—C_6H_5COOH; $C_7H_6O_2$

IX—  ; $C_{10}H_8$

X—$(CH_3)_2CHCHO$; C_4H_8O

XI—$C_6H_5C(CH_3)_2C(OH)(C_2H_5)C_6H_5$; $C_{23}H_{24}O$

XII—$CH_3C_6H_4OHCHOH$ ($C_6H_4COCH_3$); $C_{15}H_{16}O_2$

Since in the course of a study of the decomposition of more than 24 different materials only the two types of decomposition indicated were observed, it can be fairly safely assumed that combustion in the quartz test tube proceeds layer by layer and not through the whole mass of the sample of compound being burned.

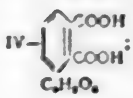
TABLE 4

Test substance	Amount, % C	Amount, % H	H/C	Test substance	Amount, % C	Amount, % H	H/C	Test substance	Amount, % C	Amount, % H	H/C
I	1,75	7,70	4,40	III	0,33	2,42	7,33	V	0,50	12,46	24,92
	1,83	10,22	5,58		0,85	9,75	11,47		0,69	12,96	18,78
	3,58	15,08	4,21		2,56	15,26	6,00		1,11	14,10	12,88
	7,40	26,28	3,55		11,17	45,86	4,10		2,94	27,50	9,37
	23,81	54,81	2,30		22,22	66,37	2,99		4,83	33,72	7,00
	47,85	82,00	1,71		61,53	92,55	1,50		6,57	35,71	5,43
	52,56	86,47	1,64		100	100	1,00		15,83	50,55	3,20
	58,18	90,19	1,55						26,62	56,70	2,10
	81,49	96,73	1,11						35,60	64,44	1,82
	100	100							80,24	87,85	1,09
									93,37	95,34	1,09
									100	100	1,00
II	4,07	65,94	16,20	IV	6,49	2,13	0,33	VI	0,12	2,34	19,50
	5,50	67,28	12,23		2,77	5,47	2,90		0,51	4,00	7,84
	14,03	70,93	5,06		12,57	22,65	1,82		1,27	5,63	4,43
	71,33	88,60	1,24		31,75	44,27	1,08		1,55	11,44	7,39
	88,93	95,38	1,07		54,37	64,99	1,19		9,45	14,82	1,57
	100	100	1,00		58,00	71,01	1,22		18,76	21,37	1,14
					69,88	75,71	1,08		31,15	33,74	1,08
					99,64	94,75	0,95		48,65	56,52	1,20
					100	100	1,00		69,37	70,13	1,01
									100	100	1,00

I–Sucrose; $C_{12}H_{22}O_{11}$

II–HOOC–COOH · $2H_2O$; $C_2H_2O_4$

III– $CH_2OHCHOHCH(-O-)COH-COHC=O$; $C_3H_4O_3$

IV–  ; $C_4H_4O_4$

V–$HOOCCH_2C(OH)(COOH)CH_2COOH \cdot H_2O$; $C_6H_{10}O_8$

VI–HOOCCH=CHCOOH $C_4H_4O_4$

SUMMARY

A study has been made of the degradation of organic compounds in a stream of oxygen; the test compounds were inserted in quartz test tubes in which the degradation was carried out, these test tubes being inserted in an empty combustion tube. It has been shown that degradation proceeds layer by layer and not throughout the whole mass of the compound.

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A MICROMETHOD FOR THE DETERMINATION OF SULFUR IN ORGANIC MATERIALS USING A NEW INDICATOR, CARBOXYARSENAZO, FOR TITRATION OF SO_4^{2-} IONS

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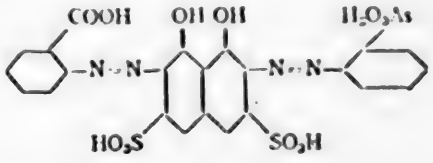
Among the methods for determining sulfur in organic compounds the ones which have found widest application are catalytic destructive hydrogenation [1], pyrolytic combustion in an oxygen stream [2], and also a number of methods which include decomposition of organic material by Schöniger's method [3-7]. When such methods are used, determination of the sulfate ion formed is usually carried out by titration with a solution of a barium salt in the presence of indicators [3-5].

A large number of organic reagents of different classes have been suggested as indicators for barium [3-5, 8-12]. Nevertheless, application of the widely used indicators for barium such as sodium alizarin sulfonate [4], thoron [5], phthalein complexon [3,8], sodium rhodizonate [10,11], stilbina[illegible]thazo [12], etc., to titration of sulfate ions is not characterized by high sensitivity and by clearly defined color changes. In this connection, a new organic reagent is suggested in the present article for the titrimetric determination of sulfur after combustion of test material by the Schöniger method; this reagent* is carboxyarsenazo, 2-phenylcarboxylic acid-(1-azo-2)-1,8-dihydroxynaphthalene-3,6-disulfonic acid-(7-azo-1)-2-phenylarsonic acid



At pH 5.5-6.5 carboxyarsenazo gives a sensitive and contrasting reaction with barium ions. The color change is from raspberry (reagent) to blue. In the work described here the sulfate ion was determined by direct titration with barium nitrate in an approximately 50% ethanolic medium.

Organic compounds of different classes containing from 8 to 35% sulfur were analyzed by the technique suggested. Experimental results are given in the table. The results were fairly satisfactory in all cases. The experimental accuracy is ± 0.25% absolute. The suggested method can be recommended as a rapid and reliable method for routine determination of sulfur in organic compounds of varying structures containing C, H, O, N, Cl, and S.

Experimental Procedure. 5-10 mg of test material was wrapped up in ashless filter paper and placed in a platinum basket attached to the stopper of the combustion flask; the paper was ignited and the stopper plus sample inserted in a flask containing 10 ml of 6% H_2O_2 and filled with oxygen.

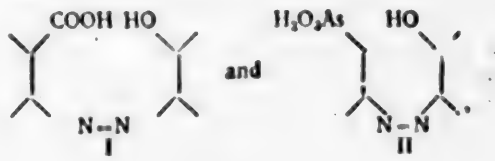
Thirty to forty minutes after combustion, the solution in the flask was evaporated down to a volume of 10 ml; it was cooled and 25 ml of ethanol and 10 ml of an acetate buffer solution with pH 5.5-5.6 were added. The solution was finally titrated with 0.02 N $Ba(NO_3)_2$ solution in the presence of two drop of a 0.3% aqueous solution of carboxyarsenazo until the violet color changed to a pale blue.

* The reagent was synthesized in CEOKhI, Academy of Sciences, USSR, by N. N. Basargin.

Test material	S content, %		Test material	S content, %	
	calc.	found		calc.	found
p-$NH_2C_6H_4SO_3H$	18,49	18,52 18,60 18,46	$CH_3SO_2N(SCCCl_3)C_6H_4CH_3$	19,13	19,31 19,35 19,24
p-$ClC_6H_4SO_2NH_2$	16,71	16,61 16,81	$C_6H_5CH_2SCH_2C_6H_5$	14,95	15,15 15,13
$(CH_3)_2NSO_2Cl$	22,37	16,66 22,35	$ClSCCl_3$	17,20	17,11 17,09 17,08
p-$NH_2C_6H_4SO_2NH_2$	18,61	18,73 18,73 18,74	Methylene blue	8,59	8,52 8,38
			$C_5H_5OCSSCH_2COOH$	35,60	35,80 35,49

The barium solution was standardized against 0.02 N H_2SO_4. Phosphates interfere with the determination.

Properties of Carboxyarsenazo. The reagent has two functional analytical atomic groups:



which occur separately in a number of reagents suggested by Kuznetsov [13,14]. In contrast to the reagent arsenazo III [15] which has two type II groups in its molecule, carboxyarsenazoforms comparatively unstable complexes with an unlimited number of metal ions, and in this connection is of interest for the complexometric determination of barium and other elements.

Carboxyarsenazo is a more suitable reagent for the titrimetric determination of sulfate ions than the reagents listed above with respect to sensitivity and definiteness of the color change in the case of barium. It should be noted that reagents having only one group I or group II do not give contrasting color reactions with barium ions, even in an alkaline medium. With respect to the stability of the complex compounds formed with the elements, carboxyarsenazo occupies an intermediate position between the reagents arsenazo and arsenazo III.

Carboxyarsenazo is a crystalline dark-violet powder, stable in the dry state and in aqueous solutions. A solution of the reagent in an acid medium has a raspberry color, while its solution in alkali is blue, and in concentrated H_2SO_4 green. The color change of the reagent in alkalis, concentrated H_2SO_4, and during complex formation with different elements is in good agreement with published results [16].

Light absorption curves of the reagent and of its compound with barium are shown in Fig. 1. The absorption curve of the complex with barium has two maxima at 590 and 650 mμ respectively. The molar extinction coefficient of the complex at pH 5.5 and 590 mμ is 29 200.

The effect of pH on the color of the reagent itself and on its complex with barium is shown in Fig. 2. The optimum conditions for titrating with carboxyarsenazo are pH 5.5-6.5 in the acid region and pH 9-10.5 in the alkaline region.

Synthesis of Carboxyarsenazo.* Carboxyarsenazo was prepared by azo coupling of the diazonium compound of anthranilic acid with chromotropic acid in a bicarbonate medium, followed by a further coupling of the isolated

* The reagent is produced by the Volkov Moskhim Plant.

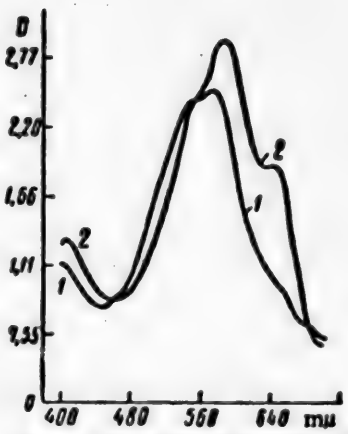


Fig. 1. Light absorption curves of a $1.8 \cdot 10^{-5}$ M solution of carboxyarsenazo (1) and of its complex with barium (2) at pH 5.5. SF-4 spectrophotometer, cell 10 mm.

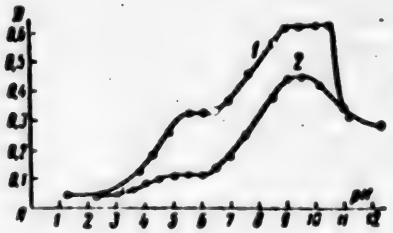


Fig. 2. Effect of pH on the development of the color of the barium-carboxyarsenazo complex (1). Barium concentration $5.4 \cdot 10^{-5}$ M. Carboxyarsenazo solution $1.8 \cdot 10^{-5}$ M (2). SF-4 spectrophotometer, cell 10 mm, λ = 650 mμ.

monoazo product [2-phenylcarboxylic acid-(1-azo-2)-1,8-dihydroxynaphthalene-3,6-disulfonic acid] with the diazonium compound of o-aminophenylarsonic acid. The second stage of the synthesis was carried out using the technique of increasing the reactivity of the material by complex formation [16].

13.02 g (0.06 M) o-aminophenylarsonic acid is dissolved in 20 ml of water and 15 ml of concentrated HCl. The solution is cooled and then diazotized by adding 4.5 g (0.065 M) $NaNO_2$ in 10 ml of water with stirring.

10.24 g (0.02 M) of the disodium salt of the monoazo product is dissolved in 70 ml of water, 1.5-1.7 g of CaO being added. First the diazo solution and then CaO (in portions of about 0.2 g, total 20 g) are added periodically to the solution obtained on cooling and stirring.

The reaction mixture, which is dark-blue in color, is stirred for 40-60 min and allowed to stand overnight. It is then acidified with 40 ml of concentrated HCl; the precipitate of the calcium salt of carboxyarsenazo is filtered off and washed with 50 ml of 6 N HCl. The yield is 14-15 g.

In order to purify the product and to convert the calcium salt of the reagent to its sodium salt, 14.5 g of the product is dissolved in 100 ml of water; 4.5-5 g Na_2CO_3 (anhydrous) is added and the solution heated and then filtered. The reagent is salted out of solution by means of NaCl. The precipitate of the trisodium salt of the reagent is filtered off and dissolved in 250 ml of water on heating. After being cooled, the solution is acidified with HCl to pH about 1, and the disodium salt of carboxyarsenazo which separates out filtered off. The yield of pure product is 11-12 g.

Carboxyarsenazo can also be obtained by a similar method by azo coupling of arsenazo with the diazonium compound of anthranilic acid.

SUMMARY

A titrimetric micromethod for the determination of sulfur in organic compounds has been developed. Test material is decomposed by the Schöniger technique in a flask filled with oxygen, and the sulfate ions formed titrated with a barium nitrate solution using a new indicator, carboxyarsenazo. The synthesis and properties of carboxyarsenazo are described. The analytical accuracy is ± 0.25% (absolute).

Phosphorus present in the test material interferes with sulfur determination.

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POLAROGRAPHIC DETERMINATION OF CAPROLACTAM AND AMINO ACIDS – INTERMEDIATE PRODUCTS IN SYNTHETIC FIBER PRODUCTION

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Aliphatic amino acids are not reduced on a dropping mercury electrode, but several indirect methods are known for their polarographic determination [1-3].

Caprolactam and amino acids–intermediate products in synthetic fiber production–have not hitherto been studied polarographically. The work described here is devoted to the development of a method for the polarographic determination of these amino acids (AA). In this method caprolactam (CL) was converted into ε-aminocaproic acid (ACA) by hydrolysis (at a concentration $C_{CL} \leq 2$ g caprolactam in 1 liter of about 1 N H_2SO_4, caprolactam is completely hydrolyzed after boiling for one hour under reflux).

Among other amino acids which are important for synthetic fiber production we studied 7-amino enanthic acid (AEA), 9-aminopelargonic acid (APA), and 11-aminoundecanoic acid (AUA).

EXPERIMENTAL*

The basis of the polarographic method which we have developed for the determination of amino acids is the reaction between amino acids and formaldehyde (F) in alkaline media [4]:

$$NH_2RCOO^- + CH_2O \overset{K_{equilib.}}{\rightleftarrows} CH_2RCOO^- + H_2O. \qquad (1)$$

The compound CH_2NRCOO^- – a so-called Schiff's Base (SB) formed as the result of the reaction is polarographically active; it gives one clearly defined polarographic wave at all values of the pH of the supporting electrolyte; the wave appears at potentials which are more positive than that of the formaldehyde wave. This is a very important factor, since a large excess of formaldehyde is used for carrying out the reaction.

It should be pointed out that Zuman [5] was the first to establish the possibility of carrying out a polarographic detection of a Schiff's Base, taking as examples the reaction between other amino acids and other aldehydes and ketones.

Reaction (1), which proceeds rapidly in an alkaline medium, has already been used several times for the alkalimetric determination of amino acids [4]. The polarographic method, however, for which, as will be shown below, neither the extent or completeness of reaction (1) toward the right hand side, nor the basicity of the Schiff's Base formed are of any significance, is superior to the alkalimetric method. In addition, the polarographic method can be applied to amino acid concentration which are appreciably lower than those that can be handled by the alkalimetric method.

Polarographic studies were carried out on an EP-312 electronic polarograph. The cell, which was fitted with an external reference electrode (saturated calomel electrode), was thermostatted at 25 ± 0.3°. Oxygen was purged with nitrogen. The capillary characteristics taken in 0.1 N H_2SO_4 at a potential of −0.9 v were: for capillary No. 1 $m^{2/3} t^{1/6} = 1.05$ $mg^{2/3} t^{-1/2}$, and for capillary No. 2 $m^{2/3} t^{1/6} = 3.16$ $mg^{2/3} t^{-1/2}$.

The purity of the amino acids used, according to the results of microanalysis, were: ε-ACA, 99%; AEA, 95.2%; APA, 94.9%. We were unable to establish the purity of AUA.

The formaldehyde used was technical grade material with an initial concentration of 32% CH_2O; its concentration was established iodometrically [6].

* S. P. Grishaeva took part in the experimental work.

Buffer solutions were prepared from Na_2HPO_4 and citric acid.

A clearly defined wave (Fig. 1) corresponding to a Schiff's Base could be observed within a few minutes of adding formaldehyde to an alkaline solution (NaOH) of the amino acids. The wave height does not change with time. This indicates that reaction 1 reaches an equilibrium state rapidly, in agreement with the results of alkalimetric studies [4]. As pointed out already, the wave is located at potentials which are more positive than that of formaldehyde. Thus, for ϵ-ACA, $E_{1/2}$ = −1.30 v in 0.1 N NaOH, while under the same conditions $E_{1/2}$ for formaldehyde is −1.59 v [7].

Thus it should be possible to carry out a polarographic determination of amino acids in alkaline solution after addition of formaldehyde. In an alkaline solution of 0.1 N NaOH, however, the constant of the limiting current is very low. In buffer solutions at pH 6-8, and in acid solutions at pH 1-2, the wave is 5-8 times greater than in 0.1 N NaOH. Taking this fact into account, we carried out most of our experiments in 0.1 N H_2SO_4 (the wave form shown in Fig. 1). In all these experiments reaction (1) was carried out in about 0.2N NaOH, after which the solution was neutralized and 0.1 N H_2SO_4 or buffer solution added. Since it was necessary to neutralize 0.2 N NaOH, and in the case of caprolactam also necessary to neutralize about 1 N H_2SO_4, the solution being polarographed also contained 0.1-0.25 N Na_2SO_4.

Fig. 1. Polarograms of the Schiff's Base from ϵ-ACA: C_{AA} = 0.885 mM/liter; C_F = 1.6%. 1) 0.1 N NaOH; 2) 0.1 N H_2SO_4 + 0.25 N Na_2SO_4.

TABLE 1. Limiting Current Constants (i_k) and Half-Wave Potentials ($E_{1/2}$) for the Schiff's Bases from Amino Acids (Capillary No. 1)

i_k, $E_{1/2}$ \ Acid	ϵ-ACA	AEA	APA	AUA
$i_k \frac{\mu a}{mM}$	0.357	0.400	0.490	0.707
$-E_{1/2}$	0.81	0.79	0.75	0.70

It was established that the wave height increases with increasing formaldehyde concentration. Accordingly, while studying the relationship between the limiting current and amino acid concentration, the formaldehyde concentration of the solution being polarographed was kept constant at 3.8%; in the alkaline solution in which reaction (1) was carried out the formaldehyde concentration was 6.1%. Although an increase in formaldehyde concentration increases the wave height, and thereby the sensitivity of the method, it is not desirable to increase the formaldehyde concentration in the solution being polarographed beyond 4-5%, since formalin often contains impurities which lead to some increase in the current in the region of the Schiff's Base wave. Bearing this in mind, in cases where the amino acid concentration is very low (hundredths of mM/liter) the supporting electrolyte should be checked polarographically.

For eliminating maxima which are only observed at high amino acid concentrations (> 5-10 mM/liter) 0.02% gelatin solution was added.

There is a linear relationship between the limiting current and amino acid concentration over a fairly wide range (Fig. 2): for ϵ-ACA from 0.038 to 35.0 mM/liter; for AEA from 0.033 to 26.2 mM/liter; for APA from 0.055 to 16.5 mM/liter; and for AUA from 0.049 to 0.49 mM/liter.

Table 1 contains the limiting current constants and the corresponding half-wave potentials, which are almost independent of the amino acid concentration. As the results in the table show, the further the amino group from the carboxyl group the greater is the shift in the half-wave potential toward the positive side, and the greater the limiting current constant.

Using the calibration curves $i_k - C_{AA}$, a large number of determinations of amino acids in solution were carried out (Table 2). The accuracy is not less than ± 3% (relative).

TABLE 2. Polarographic Determination of Caprolactam in Solution

Taken, mM/liter · 10^2	Found, mM/liter · 10^2	Error, % (relative)	Taken, mM/liter	Found, mM/liter	Error, % (relative)
9,20	9,98	−2,4	0,860	0,880	+2,3
7,25	7,15	−1,4	0,750	0,755	+0,6
10,2	10,4	+2,2	0,916	0,935	+1,6
11,9	12,2	+2,2	0,962	0,975	+1,3
6,72	6,59	−2,2	0,892	0,915	+2,6
8,14	8,35	+2,7	0,883	0,895	+1,4
11,7	11,4	−2,6	0,930	0,915	−1,6
12,9	12,6	−2,3	1,10	1,12	+1,3
8,95	9,15	+2,2	1,01	1,03	+2,0
14,6	14,5	−0,7	1,40	1,36	−2,9

TABLE 3. The Relationship Between the Limiting Current of the Schiff's Base from ε-ACA and the Height (h) of the Mercury Reservoir, and Formaldehyde Concentration (C_F) in the Solution Being Polarographed (without gelatin). C_{AA} = 0.885 mM/liter (Capillary No. 2).

C_F, %	h, cm			
	30	40	50	60
0,032	A 0,568	0,568	0,575	0,582
	B 0,104	0,0897	0,0813	0,0752
0,32	A 0,764	0,781	0,781	0,800
	B 0,139	0,122	0,111	0,103
3,2	A 1,16	1,20	1,27	1,33
	B 0,212	0,189	0,179	0,171
6,4	A 1,49	1,67	1,74	1,85
	B 0,272	0,264	0,246	0,238
12,8	A 1,93	2,11	2,25	2,38
	B 0,352	0,334	0,318	0,304
19,1	A 2,04	2,18	2,32	2,47
	B 0,372	0,344	0,328	0,319
25,5	A 2,14	2,25	2,44	2,51
	B 0,391	0,356	0,345	0,324

Notes: A = i_k, μa; B = $i_k/\sqrt{h}$, μa·cm$^{-\frac{1}{2}}$

RESULTS

There is no direct relationship between the limiting current and the square root of the height of the mercury reservoir; this indicates that the limiting current is kinetic in character. The kinetic character of the limiting current (Tables 3,4) is maintained on increasing the formaldehyde concentration, and also at varying pH.

The results obtained enable one to advance some hypotheses regarding the mechanism of the development of the polarographic wave of a Schiff's Base.

As noted already, in an alkaline medium reaction (1) finishes by rapid establishment of an equilibrium with an equilibrium constant $K^{\bullet}_{equilib.}$ In an acid medium of 0.1 N H_2SO_4, presumably because of the conversion of the amino group into NH_3^+, a Schiff's Base is not in general formed; this also explains the absence of a wave on adding formaldehyde directly to an acid solution.

On the basis of [8] we assume that only nonhydrated formaldehyde participates in the reaction with the amino group. Taking into account the equilibrium

$$CH_2O + H_2O \overset{K^{\bullet}_{equilib.}}{\rightleftarrows} CH_2(OH)_2, \qquad (2)$$

TABLE 4. Effect of pH of the Buffered Supporting Electrolyte (without gelatin) and the Height (h) of the Mercury Reservoir on the Polarographic Characteristics of the Schiff's Base from ε-ACA; C_{AA} = 0.885 mM/liter; C_F = 1.6% (Capillary No. 2)

1) h, cm.

h, cm	30		40		50		60		—%
pH	A	B	A	B	A	B	A	B	
1,0*	0,93	0,170	0,97	0,153	0,98	0,139	1,00	0,129	0,75
2,2	0,87	0,159	0,93	0,147	0,97	0,137	1,00	0,129	0,75
3,1	0,49	0,0898	0,53	0,0840	0,57	0,0805	0,58	0,0750	0,76
3,6	0,37	0,0677	0,40	0,0633	0,44	0,0622	0,44	0,0569	0,80
5,2	0,58	0,106	0,60	0,0950	0,62	0,0876	0,64	0,0826	0,89
5,2	0,75	0,137	0,78	0,123	0,82	0,116	0,86	0,111	0,92
6,7	1,13	0,206	1,13	0,179	1,17	0,165	1,17	0,151	0,94
7,3	1,46	0,267	1,43	0,226	1,50	0,212	1,54	0,199	0,98
7,8	1,65	0,302	1,65	0,261	1,72	0,243	1,72	0,222	1,01
8,2	—	—	—	—	—	—	1,58	—	1,07
9,5	1,12	0,205	1,16	0,183	1,20	0,170	1,25	0,161	1,09
13,0**		—	—	—	—	—	0,19	—	1,30

Note: A = i_k, μa; B = $i_k/\sqrt{h}$, μa·cm$^{-\frac{1}{2}}$.

*0.1 N H_2SO_4.

**0.1 N NaOH.

and also that the total formaledehyde concentration (C_F) is very much greater than the total concentration of amino acid (C_{AA}), the concentration of the Schiff's Base (C_{SB}) can be expressed by:

$$C_{SB} = \frac{K_{equilib.} C_{AA} \cdot C_F}{1 + K_{equilib.} \cdot C_F} \tag{3}$$

where

$$K_{equilib.} = K^{\circ}_{equilib.} \frac{1}{K^{\circ}_{equilib.} + 1}. \tag{4}$$

As indicated already, the polarographic wave of the Schiff's Base has a kinetic character. This is explained by the fact that the chemical reaction proceeds on the electrode surface. The nature of this reaction has not yet been explained.

Assuming the monomolecularity of the limiting s age of the electrode process with respect to the Schiff's Base, we obtain on the basis of the theory of kinetic currents [9,10]:

$$i_k = a\mu_1 k_1 C^s_{SB}$$

$$k_d (C_{SB} - C^s_{SB}) = a\mu_1 k_1 C^s_{SB}. \tag{5}$$

$$a = nFq \cdot 10^{-3} \tag{6}$$

where i_k is the limiting current; q is the mean surface of the mercury drop; n is the number of electrons in the electrode reaction; μ_1 is the thickness of the reaction layer; C^s_{SB} is the concentration of the Schiff's Base on the electrode surface; k_1 is the velocity constant of the limiting chemical stage of the electrode process; and k_d is the diffusion current constant of the Schiff's Base.

Solving equation (4), (5), and (6) simultaneously, we obtain:

$$i_k = \frac{K_{equilib.} \cdot k_d \cdot C_{AA} \cdot C_F}{\left(1 + \frac{k_d}{a\mu_1 k_1}\right)(1 + K_{equilib.} \cdot C_F)}. \tag{7}$$

It follows from equation (7) that at C_F = const, and for a given height (h) of the mercury reservoir, there should be a linear relation between the limiting current and the amino acid concentration; as we have already seen this is confirmed experimentally.

Thus, amino acids can be determined polarographically even when the yield of a Schiff's Base by reaction (1) is considerably less than 100%. It is assumed of course that the equilibrium of reaction (1) in 0.1 N H_2SO_4 is not shifted during the life of a mercury drop [8]. Moreover, as will be shown below, it can be assumed that after rapid neutralization and acidification of the alkaline solution, the equilibrium of reaction (1) will be "frozen."

Since $\frac{k_d}{\sqrt{h}}$ is independent of h, then the equation $i_k = f(h, C_F)$ at C_{AA} = const will assume the form:

$$i_k = \frac{A\sqrt{h}\cdot C_F}{(1 + B\sqrt{h})(1 + K_{equilib.}C_F)}, \tag{8}$$

where

$$A = K_{equilib.}\cdot\frac{k_d}{\sqrt{h}}\cdot C_{AA}, \tag{9}$$

$$B = \frac{k_d}{\sqrt{h}\,a\mu_1 k_1}. \tag{10}$$

In the case of ε-aminocaproic acid, equation (8) is in good agreement with experimental results over a fairly wide formaldehyde concentration range, and for appreciable changes in the height of the mercury reservoir (Table 5). The following values were found in this case: A = 120, B = 1.2, and $K_{equilib.}$ = 103. Calculations showed that equation (7) is in considerably better agreement with experimental data if the formaldehyde concentration in the alkaline medium (0.2 N NaOH) is taken into account rather than its concentration in the solutions being polarographed (0.1 N H_2SO_4). The formaldehyde concentration given in Table 5 correspond to those in alkaline solutions. This

TABLE 5. Comparison of Experimental and Calculated Limiting Currents for the Schiff's Base from ε-ACA; C_{AA} = 0.885 mM/liter (Capillary No. 2)

h, cm	30		40		50		60	
C_F, mM/liter	i_k, μa							
	measured	calculated	measured	calculated	measured	calculated	measured	calculated
$1.75\cdot10^{-3}$	0,54	0,54	0,57	0,55	0,58	0,56	0,58	0,56
$2.42\cdot10^{-3}$	0,61	0,60	0,61	0,61	0,61	0,62	0,63	0,63
$3.00\cdot10^{-3}$	0,63	0,64	0,63	0,65	0,64	0,66	0,64	0,66
$3.51\cdot10^{-3}$	0,66	0,66	0,68	0,67	0,69	0,68	0,68	0,69
$9.52\cdot10^{-3}$	0,73	0,77	0,75	0,78	0,73	0,79	0,75	0,80
0.137	0,77	0,79	0,77	0,80	0,77	0,81	0,78	0,82
0.175	0,77	0,80	0,77	0,81	0,77	0,82	0,79	0,83
0.300	0,82	0,82	0,84	0,83	0,84	0,84	0,88	0,85
0.962	0,93	0,83	0,97	0,85	0,98	0,86	1.00	0,87

result indicates that the equilibrium in reaction (1) is "frozen" after neutralization and acidification of the alkaline solution. A similar phenomenon could be predicted from [8], which shows that the velocity constants of the forward and reverse reactions of urea with formaldehyde are sharply depressed on shifting the pH to the acid region.

It follws from equation (7) that at high values of C_F (C_F > 1 M), i_k should not depend on C_F. It has been shown experimentally, however, that the growth of i_k with increase in C_F continues even when C_F is considerably greater than 1 M (Table 3). It is possible that this can be explained by the partial influence at high formaldehyde concentrations of the reaction between amino acid and hydrated formaldehyde (which is polymerized to some extent at C_F > 1 M).

It is of interest to note that the values of A=120 and $K_{equilib.}$=103 are in good agreement with equation (9).

if one assumes the reaction to be a two-electron process, and the diffusion coefficient of the Schiff's Base from ε-aminocaproic acid is calculated from the mobility of the caproate anion [11]. Presumably, therefore, reduction proceeds across the double bond with formation of methylaminocaproic acid. There is a published reference [12] to the reduction of the Schiff Base CH_2NCH_2COOH by hydrogen in an acid medium to methylaminoacetic acid CH_3NHCH_2COOH.

From the value of $K_{equilib.} = 103$ it is possible to calculate $K'_{equilib.}$, the equilibrium constant for process (1), in the case of the interaction of ε-aminocaproic acid with formaldehyde in 0.2 N NaOH. For this purpose we calculated $K_{equilib.} = 1.4$ (process II) on the basis of the results given in [8] (0.05 N LiOH, 25°). Substituting $K_{equilib.} = 103$ and $K^*_{equilib.} = 1.4$ in equation (4) we found that $K_{equilib.} = 250$. This value indicates that even in a 1 M formaldehyde solution the yield of a Schiff's Base is almost 100%. The increase in yield of a Schiff's Base from glycine with increasing formaldehyde concentration was noted in [13]. Determination of the value of the equilibrium constant of process (1) is of great importance for the practical application of the alkalimetric method of determining amino acids.

It was pointed out above that the limiting current constant (see Table 1) is greater the further the amino group is removed from the carboxyl group in the amino acid molecule. Since under these conditions in reaction (1), the formaldehyde concentration was sufficiently high (about 6%), and bearing in mind that for ε-ACA, $K_{equilib.} = 103$, the reason for the growth of i_k must be the increase in the velocity constant of the limiting chemical stage in the series: ε-ACA, AEA, APA, and AUA. Since the basicity of the nitrogen in this series increases, one cannot exclude the possibility that the limiting stage is the addition of a proton on the nitrogen atom.

The relation between i_k and pH (see Table 4), which could throw light on the limiting chemical state of the electrode reaction, was a very complex one. Over the pH range 1-2, i_k = const; subsequently i_k drops with increasing pH. At pH > 4, i_k starts to increase, while at pH > 8 there is a sharp drop in i_k. Presumably, such a complicated character of the i_k – pH relationship can be explained by the simultaneous effect of pH in different directions: both on equilibrium (1) (at pH's close to 7 and greater than 7) and on the kinetics of the electrode process.

Finally we should like to point out that the possibilities of the polarographic detection of Schiff's Bases may be widely used in the chemistry of polymers, including the analysis of proteins.

SUMMARY

Methods have been developed for the polarographic determination of caprolactam in the form of ε-aminocaproic acid, and also for the determination of other amino acids by their rapid conversion (0.2 N NaOH) into polarographically active Schiff's Bases (reaction with formaldehyde) which give one clearly defined wave at all pH values of the supporting electrolyte. This wave occurs at potentials which are more positive than that of the formaldehyde wave.

A linear relationship has been established between the limiting current and total amino acid concentration (0.1 N H_2SO_4). The limiting current constant increases in the series ε-aminocaproic acid; 7-aminoenathic acid; 9-aminopelargonic acid; 11-aminoundecanoic acid. The half-wave potentials are shifted to more positive values in the same succession; the limiting current is kinetic in character.

On the basis of data obtained during a polarographic study of the Schiff's Base obtained from ε-aminocaproic acid, a quantitative evaluation has been made of the effect of formaldehyde concentration and the height of the mercury reservoir on the value of the limiting current. The equilibrium constant of the reaction between ε-aminocaproic acid and formaldehyde has been determined.

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BRIEF COMMUNICATIONS

PURIFICATION OF CERTAIN QUATERNARY AMMONIUM COMPOUNDS USED IN POLAROGRAPHY

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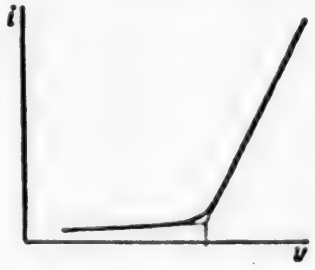
Tetraalkylammonium compounds used as supporting electrolytes in polarography have to meet very strict purity requirements. These compounds should be purified even from trace amounts of impurities which give polarographic waves or catalytically depress the hydrogen overvoltage on a dropping mercury cathode. Vecek [1] has suggested difficult and complicated methods of purifying tetramethylammonium chloride and iodide by repeated crystallization from alcoholic solution using the tetramethylammonium base obtained by means of silver oxide. Another method [2] of purifying tetramethylammonium chloride by means of methanol and acetone can only be carried out by using completely anhydrous solvents. A method has also been published for purifying tetrabutylammonium iodide [3].

In the work described here the extent to which the quaternary ammonium salts have been purified was assessed polarographically on the basis of the potential value (relative to the saturated calomel electrode) at which interfering waves start to appear in a 0.1 N aqueous solution of the test material, the potential being determined graphically (see figure). Numerous experiments showed that the potential value determined in this way is independent of the chosen sensitivity of the galvanometer and can characterize the purity of the solution. An LP-55 polarograph was used at a sensitivity of S = 1/10 – 1/100; the dropping period of the capillary was 6 sec at zero applied potential.



The method used for establishing the potential at which interfering waves start to appear.

Contact between the solution and a saturated calomel electrode was established via an electrolytic bridge 1/3 filled with a 2% gel of agar-agar prepared in a 0.2 N aqueous solution of $(C_2H_5)_4NI$, and 2/3 filled with saturated KCl solution. At high galvanometer sensitivities oxygen was purged from solution with nitrogen.

Many quaternary ammonium salts are very readily soluble in water [$(CH_3)_4NI$ is sparingly soluble], so that recrystallization from aqueous solutions is usually complicated because of the low yield of purified product. Accordingly, purification techniques were developed in which two organic solvents were used, the two solvents chosen being such that the purified material is readily soluble in one of them and sparingly soluble in the other (Table 1). Using such a technique it was found possible to purify three of the quaternary salts studied in similar fashion, the only difference being the nature of the solvents used. According to this technique, 10 g of the salt to be purified is dissolved in the solvent indicated; the solution is filtered and a precipitant added to the filtrate; the precipitate is collected on a filter, washed, and finally dried in a vacuum desiccator. Results are given in Table 2.

The solubility of tetramethylammonium iodide increases sharply with rising temperature [4]; the salt can be purified by recrystallization from water in this way. Thirty g of $(CH_3)_4NI$ is dissolved in 100 ml water on boiling; the hot solution is filtered; and the crystals which separate out on cooling are filtered off from the mother liquor, washed with cold water, and dried. The salt is then redissolved in 100 ml of boiling water and poured into a glass beaker contained in a large vessel containing water heated to 100°, after which it is left overnight for slow cooling. The crystals which separate out are filtered off, washed, and dried. The yield is 50%. The mother liquors can be evaporated down to recover the salt. When the method described was used, starting with a salt for which the potential at which interfering waves started to appear was –2.05 v, a product was obtained for which the corresponding potential was –2.3 v; this product is suitable for the polarographic determination of potassium and sodium.

A more careful purification can be carried out by prolonged extraction of tetramethylammonium iodide with chloroform. For this purpose the salt which has been purified by recrystallization from water is dried, ground, and

TABLE 1. Solubility of Tetraalkylammonium Salts in Water and in Some Organic Solvents

Test material	Water	Methanol	Ethanol	Acetone	Ethyl ether	Chloroform
Tetramethylammonium chloride $(CH_3)_4NCl$	Soluble	Soluble	Soluble	Insoluble	Insoluble	Insoluble
Tetramethylammonium bromide $(CH_3)_4NBr$ *	55 (15°)		Sparingly soluble	•		•
Tetramethylammonium iodide $(CH_3)_4NI$	4.2 (20°) 43 (95°)	0.5 (20°) 1.0 (60°)	0.025	•	•	•
Tetraethylammonium chloride $(C_2H_5)_4NCl$	141 (25°)	Soluble	Soluble	Soluble		Soluble
Tetraethylammonium bromide $(C_2H_5)_4NBr$	Soluble	•	•	•	Soluble	•
Tetraethylammonium iodide $(C_2H_5)_4NI$	45 (25°)	•	2.9 (27°)	Insoluble	Insoluble	0.87 (20°)

* The values quoted refer to the solubility in g per 100 g of solvent. Results for $(CH_3)_4NBr$ and $(C_2H_5)_4NCl$ are taken from Dictionary of Organic Compounds, 1949, IL, Moscow, pp. 689 and 721.

TABLE 2. Purification of Tetralkylammonium Salts

Material to be purified	Solvent	Precipitant	Washed on the filter with:	Yield, %	Potential at which interfering waves start to appear, v (relative to the saturated calomel electrode)	
					Original material	Purified material
Tetramethylammonium chloride	Mixture of 50 ml methanol and 100 ml chloroform	200 ml ether	50 ml ether	75	−2.3	−2.6
Tetraethylammonium bromide	50 ml chloroform	100 ml benzene	50 ml benzene	80	−2.2	−2.8
Tetraethylammonium iodide	Mixture of 5 ml methanol and 100 ml chloform	50 ml benzene	50 ml ether	65	−2.35	−2.75

100 ml of chloroform added to it. After extraction for 7-10 days with periodic stirring, the salt is transferred to a filter, washed with 50 ml of chloform, dried, and recrystallized from water on slow cooling. Chloroform treatment can be replaced by a water extraction (300 ml of water) over a period of one month.

In aqueous solutions of a salt purified in this way the potential at which the hydrogen wave starts to appear is −2.65 v. Recrystallization of $(CH_3)_4NI$ from methanol does not give satisfactory results.

SUMMARY

New methods have been developed for purifying tetramethylammonium chloride and iodide, and tetraethylammonium bromide and iodide. The purified products can be used for polarographic determinations in extremely negative potential regions.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

THE INCREASE IN THE SENSITIVITY OF THE POLAROGRAPHIC DETERMINATION OF URANIUM IN THE PRESENCE OF VANADIUM AND PHOSPHATE IONS

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Starik et al.[1] and later Sinyakova [2] and other research workers have pointed out the considerable influence which vanadium compounds exert on the polarographic reduction current of UO_2^{2+}. The nature of this phenomenon was first studied and explained by Sochevanov and Shmakova in 1953, and was subsequently confirmed by Morachevskii and Sakharov [3].

When the vanadium content of the solution is unknown, quantitative polarographic determination of uranium is impossible. When, on the other hand, the vanadium concentration of the solution is established at a constant level, this has a beneficial effect on the determination of uranium, because of an increase in the polarographic current of uranium to ten times and more, and because of the increased sensitivity of determination.

During polarographic determination of uranium in synthetic solutions containing vanadium, it was established that good results can be obtained in a chloride medium which is 0.5 M with respect to HCl and 1 M with respect to chloride ions. The vanadium can be conveniently introduced into solution in the form of a concentrated solution of sodium vanadate.

A solution which has a constant concentration relative to H^+ and Cl^- is prepared by adding 2 ml of concentrated HCl to a known volume of a standard solution of uranyl chloride contained in a 25-ml standard flask, and then adding a known volume of sodium vanadate solution. The orange colored solution is reduced on heating to 40-50° with the minimum amount of ascorbic acid. Completion of reduction is readily observable by the appearance of a pure blue color. To the solution obtained in this way is added 0.6 ml of 10 M NaOH and 10 drops of 0.1% thymol solution, after which the volume is made up to the mark with water and the whole thoroughly mixed. After an aliquot of the solution has been purged with hydrogen or CO_2, it is polarographed over the polarization voltage range 0.0-0.4 v (saturated calomel electrode).

Polarographic waves for uranium before and after addition of vanadium are compared in Fig. 1. Figure 2 shows the relation between the wave height for the reduction of uranium and the concentration of quadrivalent vanadium in solution. It is clear from these curves that vanadium strongly affects the wave height of uranium.

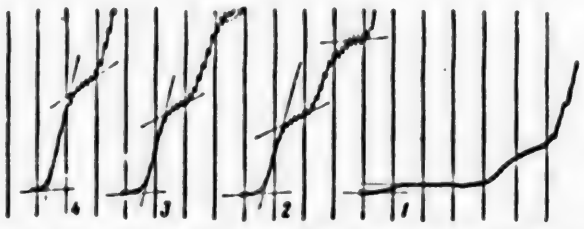

Fig. 1. Effect of vanadium on the polarographic wave of uranium when the concentration of the latter is 10^{-4} M. Vanadium concentration, M: 1) 0; 2) 4×10^{-3}; 3) 5.6×10^{-3}; 4) 8.0×10^{-3} M UO_2^{2+}.

At high vanadium concentrations, oscillations increase and the uranium wave starts to fuse with the wave for the reduction of the trivalent vanadium ions formed.

Phosphoric acid is added to the solution to improve the upper section of the uranium wave and to eliminate the wave of trivalent vanadium; phosphoric acid depresses the uranium wave to some extent, but it depresses or leads to the complete disappearance of the trivalent vanadium wave (Fig. 3 and table).

The linear nature of the relationship between the uranium wave height and phosphoric acid concentration

Phosphoric acid concentration, M · 10^4	Uranium wave ht. h		$h_0 - h_x$	$\frac{h_0 - h_x}{c} \cdot 10^{-4}$
	mm	%		
0,00	25,0	100	—	—
2,21	24,0	95,0	5,0	2,26
4,42	22,8	91,2	8,8	1,98
6,53	21,2	84,9	15,1	2,28
8,84	20,3	81,2	18,8	2,13
11,05	19,0	76,0	24,0	2,17
14,47	16,5	66,0	34,0	2,35
		Mean	2,21·10⁻⁴	

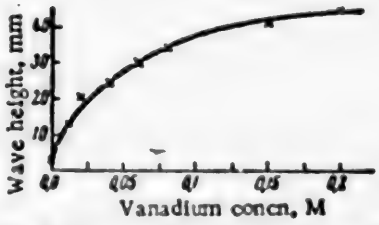

Fig. 2. The relationship between uranium wave-height and the vanadium concentration of the solution

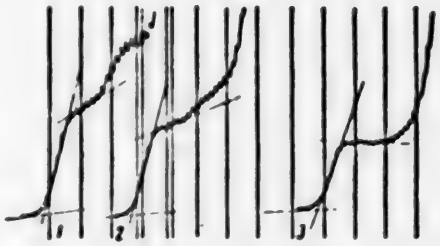

Fig. 3. Effect of phosphoric acid on the wave height of uranium when the concentration of the latter is 10^{-4}M, in the presence of vanadium at a concentration of 8×10^{-2}M. H_3PO_4 concentration, M: 1) 0.0; 2) 0.2×10^{-3}; 3) 1.11×10^{-3}.

indicates that it could be used for an indirect polarographic determination.

Uranium is determined polarographically in a supporting electrolyte of the following composition: 0.5 M with respect to HCl, 1.0 M with respect to chloride, 0.08 M with respect to vanadium, 1.0×10^{-3}M with respect to phosphoric acid, and 0.002% with respect to thymol.

The wave height is proportional to uranium content over the range 0.0 to 2.0 mg in 25 ml of solution, or from 0.0 to 3.36×10^{-4}M.

Fe^{III}, Pb, Cu, etc., which usually interfere, should be removed beforehand during determination of uranium in complex mixtures. For example, good results are obtained by precipitating ammonium diuranate from a complexon-containing solution on a column packed with silica gel [4].

SUMMARY

It has been found that the shape of the polarographic wave of uranium, which is catalyzed by quadrivalent vanadium ions, improves in the presence of phosphate ions.

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PHOTOMETRIC DETERMINATION OF CERIUM

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Photometric methods are used for the determination of small amounts of cerium in minerals and cerium-containing alloys; these methods include the peroxide [1], benzidene [2], 8-hydroxyquinoline [3], citrate [4], o-tolidine [5], etc., photometric methods. We have developed a rapid photometric method for the determination of small amounts of cerium, which does not involve separating it from a number of accompanying elements; the method is based on the oxidation – reduction interaction between quadrivalent cerium and the halochromic compound of an azo dye with sulfuric acid [6].

Of a number of azo dyes tested for this purpose, methyl orange and methyl red proved to be the most suitable.

The methyl orange solution should be prepared in 60% H_2SO_4, while the methyl red solution should be prepared in 80% H_2SO_4; the absorption maximum of the first solution occurs at 496 mμ, while that of the second lies at 533 mμ. Both dyes give almost identical results; accordingly, we shall only give the results obtained when methyl red was used.

With addition of increasing amounts of quadrivalent cerium salts to a sulfuric acid solution of methyl red, the optical density of the dye solution decreases. When the difference D_0-D_c is plotted along the ordinate and the cerium concentration (in μg/ml) plotted along the abscissa, a curve in the form of an ascending straight line is obtained (figure).

This relation is expressed mathematically by the equation for a straight line $D_0-D_c = KC$, where D_0 is the optical density of the dye solution (free from cerium), D_c is the optical density of the dye solution after addition of C μg cerium per ml of solution, and K is the proportionality coefficient.

Preparation of Solutions for Constructing a Calibration Curve. 0.0202 g of $Ce(SO_4)_2 \cdot 4H_2O$ is dissolved in 2 N H_2SO_4 in a 250-ml standard flask; 1 ml of this solution contains 28 μg of cerium. A 10^{-4} - $3 \cdot 10^{-4}$ M solution of methyl red is prepared by dissolving the reagent in an 80% by volume aqueous solution of chemically pure sulfuric acid; if the sulfuric acid contains appreciable amounts of oxidizing impurities it should be treated with a 0.05 N $KMnO_4$ solution (the first drops are immediately decolorized on mixing; the treatment is stopped when the rose color persists for 3-5 sec).

Three ml of dye solution is introduced into each of 6 test tubes; to the first test tube is added 1 ml of the cerium salt solution, while 1.5 ml is added to the second, 2.0 ml to the third and so on; 4 ml of 2 N H_2SO_4 is added to the sixth test tube; the volumes of the solutions in test tubes 1-5 are also made up to 7 ml with 2 N H_2SO_4. The solutions are mixed and the optical density measured after 10-15 min.

TABLE 1. Data for Construction of a Calibration Curve

D_0	D_0	D_0-D_c	C, μg Ce^{IV}/ml
2,00	1,85	0,15	4
	1,70	0,30	6
	1,55	0,45	8
	1,35	0,65	10
	1,20	0,80	12

The optical densities obtained D_0 (sixth test tube) and D_c, and C (μg) are given in the table (see Table 1). A calibration curve is constructed within the coordinates D_0-D_c and C on the basis of these results.

In order to determine the cerium content of the test solution 1 ml of this solution is added to 3 ml of dye solution; the volume is made up to 7 ml with 2 N H_2SO_4 and the solution mixed; its optical density D_c is measured after 10-15 min, and the difference D_0-D_c determined; on the basis of this difference, and using the calibration curve, the cerium content in μg corre-

sponding to each ml in the final volume (7 ml) is established.

Ni^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Mg^{2+}, Al^{3+}, Cr^{3+}, MoO_4^{2-}, UO_2^{2+}, Cu^{2+}, and Co^{2+} in amounts of 1000 μg per 6 μg of cerium do not interfere with cerium determination; neither do Fe^{3+}, Cl^-, and NO_3^- interfere as long as not more than 50-100 μg of each of these ions is present per 6 μg of cerium.

Results for the determination of cerium in the presence of all the ions listed above are given in Table 2.

TABLE 2. Determination of Cerium in the Presence of Other Ions (6.0 μg Ce taken)

Me added, μg	Ce^{IV} found, μg	Deviation, μg
Cu^{2+}, Co^{2+}, Ni^{2+}, Mg^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Cr^{3+}, Al^{3+} MoO_4^{2-}, UO_2^{2+} 1000 μg of each	6.5; 5.5; 6.5 6.0; 6.2; 6.5 6.2; 5.5; 6.0	0.5; 0.5; 0.5 0.0; 0.2; 0.5 0.2; 0.5; 0.0
Fe^{3+}, Cl^-, NO_3^- 100 μg of each		

SUMMARY

A photometric method is suggested for the determination of small amounts of cerium by means of a sulfuric acid solution of methyl red; the method is based on the oxidation–reduction reaction of the azo dye with quadrivalent cerium. The decrease in the optical density of the azo dye solution is linearly related to the amount of cerium added to the solution.

Moderate amounts of Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}, Mg^{2+}, Cd^{2+}, Cr^{3+}, Al^{3+}, Fe^{3+}, MoO_4^{2-}, UO_2^{2+}, Cl^-, and NO_3^- do not interfere with cerium determination.

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DETERMINATION OF RHENIUM IN ALLOYS

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Small amounts of rhenium in alloys can be determined photometrically by the thiocyanate method [1]; ions which possess an intrinsic color or which form sparingly soluble or colored compounds interfere in this method. Copper ions form a sparingly soluble thiocyanate. We have succeeded in determining rhenium in solutions containing not more than $8 \cdot 10^{-5}$ g-ion copper/liter. Thiourea complexes copper into a colorless complex and permits determination of rhenium in the presence of $2 \cdot 10^{-3}$ g-ion copper/liter. At high thiourea concentrations a rhenium thiourea complex is formed which has different properties than the thiocyanate compound [2].

For determination of rhenium in alloys by the thiocyanate method we separated rhenium from the other components beforehand by ion exchange chromatography. Rhenium is not held back by cation exchange resins and passes into the filtrate; the cations remain on the ion-exchange column [3,4]. The cations which remain on the column can be subjected to subsequent separation or can be eluted completely into solution. Nitrates, which interfere with rhenium determination, are removed by a double evaporation of the solution with hydrochloric acid.

An iron-based alloy containing large amounts of aluminum, manganese, nickel, and up to 15% copper was analyzed. 0.1 g of alloy is dissolved in 10 ml of an acid mixture consisting of 5 ml of hydrochloric acid (1 : 2) and 5 ml of nitric acid (1 : 1). Solution is effected on gentle heating, and the solution is evaporated to a volume of 0.5-1 ml on a water bath. Evaporation should be carried out carefully since rhenium compounds are volatile from acid solutions. To the residual solution is added 5 ml of concentrated hydrochloric acid and the evaporation is repeated. Evaporation with hydrochloric acid is repeated once again. The salts are dissolved on stirring in 50 ml of distilled water. The solution obtained is passed through an ion-exchange column at a rate not exceeding 4 ml/min. For complete removal of rhenium anions it is sufficient to wash the column with 150 ml of water. The filtrate and wash liquors containing all the rhenium are collected in a 250-ml standard flask. The cations remaining on the column are eluted by washing the column with 200 ml of 4 N sulfuric acid. The acid solution containing all the cations can be used for their determination. Separation of rhenium from the other alloy components by the recommended technique takes up to 50 min.

A 50-ml buret containing 10 g of the cation exchange resin KU-2 serves as the ion-exchange column. The resin is kept in position in the buret with a plug of glass wool. The cation exchange resin is converted into the H form by successive washing of the column with 100 ml of 2 N hydrochloric acid and 100 ml of distilled water.

The rhenium solution in the standard flask is made up to the mark with distilled water. 5-10 ml of this solution is transferred to a 50-ml standard flask; 20 ml of hydrochloric acid (1 : 1) is added, followed by 2 ml of a 50% potassium thiocyanate solution and 2 ml of a 20% solution of $SnCl_2 \cdot 2H_2O$ in concentrated hydrochloric acid, and the volume made up to the mark with distilled water. The solution is mixed after addition of each reagent. The optical density is measured after 10 min in a FÉK-M photoelectrocolorimeter fitted with a blue filter; distilled water is used as the reference. The rhenium content is determined by means of a calibration curve constructed with the aid of pure potassium perrhenate.

The standard solution is prepared by dissolving 0.1554 g of potassium perrhenate in 100 ml of 1 N hydrochloric acid; 1 ml of this solution contains 1 mg of rhenium. Solutions of the requisite concentration are obtained by diluting this standard solution.

Direct photometric determination with thiourea [2] was studied as a possible way of speeding up and simplifying the determination of rhenium in alloys. In acid solutions in the presence of a reducing agent, thiourea forms with rhenium compounds a complex compound which has a greenish color. The maximum absorption of the complex

lies in the short-wavelength region of the spectrum. The relation between optical density and concentration is linear over a wide concentration range (5-160 μg Re in 25 ml). The molar extinction coefficient of the rhenium - thiourea complex is $6.2 \cdot 10^3$.

Formation of the thiourea complex is slow at room temperature. Dissolution of the alloy and evaporation of the nitric acid are carried out as decribed in the previous instance. Fifty ml of distilled water is added to the evaporated solution, and mixing carried out until the salts dissolve. The contents of the beaker used are transferred to a 200-ml standard flask and the volume made up to the mark with distilled water. A 25-ml aliquot of the solution is transferred to a 50-ml standard flask; 10 ml of concentrated hydrochloric acid is added and the solution cooled; 10 ml of a 5% aqueous solution of thiourea is added; this is followed by 2 ml of 20% $SnCl_2 \cdot 2H_2O$ solution, and the volume finally made up to the mark with water. Optical density is measured using a light filter with maximum transmission at 400 mμ.

Results of Rhenium Determination

Wt. of alloy, g	Rhenium found, %	
	by the thiourea method	by the thiocyanate method after chromatographic separation
0,103	0,58	0,60
0,113	0,64	0,61
0,120	0,60	0,59
0,133	0,61	0,61
0,144	0,65	0,62
0,161	0,61	0,62

Results of rhenium determination by the two recommended methods are given in the table.

SUMMARY

Small amounts of Re in alloys can be determined by the thiocyanate method after preliminary separation of rhenium by means of a cation exchange resin.

Direct photometric determination of rhenium as its thiourea complex is more rapid.

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SEPARATION OF IRON FROM COBALT BY MEANS OF CUPFERRON DURING SOIL ANALYSIS

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Cobalt cupferronate is readily extracted from an aqueous layer by chloroform at pH about 2, while iron cupferronate is extracted quantitatively by the same solvent at pH <1. The technique for separating iron from cobalt reduces to the following. Hydrochloric acid is added to the test solution contained in a separation funnel until the acid concentration is approximately 1 M; the volume of the solution should be 10-15 ml. Seven ml of a 6% aqueous solution of cupferron is then added in the cold; the solution is mixed and is then shaken up with 10 ml of chloroform. The chloroform layer, which has a red color from the iron cupferronate, is discarded; 3 ml of cupferron solution is added, followed by 5-7 ml of chloroform. Extraction with chloroform in the presence of cupferron is repeated until the chloroform layer has a yellow color.

The aqueous phase is evaporated to dryness on a water bath. If the dry residue has a yellow color because of the presence of cupferron, the latter is destroyed with a mixture of nitric acid and hydrogen peroxide (3 : 1) with addition of a few drops of sulfuric acid.

To determine the cobalt, the solution obtained is evaporated to dryness on a water bath. The residue is dissolved in 10 ml of a mixture of 0.5 ml of concentrated hydrochloric acid, 0.5 ml of concentrated nitric acid and 9 ml of water. The solution, which is heated to the boil, is mixed with 5 ml of a 50% sodium acetate solution and 2 ml of a 0.1% solution of nitro-R-salt, and the whole boiled for not less than one minute. Two ml of concentrated HNO_3 is added to the mixture obtained and the whole boiled again for one minute. The red colored solution is diluted to a known volume and the color of the final solution compared visually in a colorimeter tube with a scale prepared beforehand.

TABLE 1. Determination of Cobalt after Removal of Iron with Cupferron

Taken		Ratio between $Co^{2+}:Fe^{3+}$	Co^{2+} found		Taken		Ratio between $Co^{2+}:Fe^{3+}$	Co^{2+} found	
Co^{2+}, μg	Fe^{3+}, mg		μg	%	Co^{2+}, μg	Fe^{3+}, mg		μg	%
10	10	1 : 1000	9,5	95	30	20	1 : 666	29,5	98,2
15	30	1 : 2000	14,5	96,5	40	60	1 : 1500	39	97,5
20	10	1 : 500	19	95	50	30	1 : 600	48,5	97
25	50	1 : 2000	24	96	50	50	1 : 1000	49	98
30	10	1 : 333	29	96 57					

As the results given in Table 1 show, determination of cobalt after removal of iron by means of cupferron gives completely satisfactory results.

Determination of cobalt in soils gave encouraging results. For this purpose varying amounts of iron and cobalt salts were added to an aliquot of soil (5 g). The soil was calcined in a porcelain crucible in a muffle at a weak red heat for 1.5-2 hr. The crucible was cooled and 10 ml of concentrated HCl and 10 ml of concentrated HNO_3 added. The solution was evaporated to dryness on a water bath. The residue was dissolved in 20 ml of 1 M hydrochloric acid and filtered. The filtrate was transferred to a separating funnel and the iron removed by means of cupferron as described above.

TABLE 2. Determination of Cobalt in Soil (5 g) after Removal of Iron

Added		Co^{2+} found		Added		Co^{2+} found	
Co^{2+}, μg	Fe^{3+}, mg	μg	%	Co^{2+}, μg	Fe^{3+}, mg	μg	%
—	—	15,0		20	5	34,0	95,0
—	—	14,5		23	8	36,5	93,48
—	1	15,3		25	9	40,0	100,0
15	2	29,5	96,66	30	10	41,0	96,66
18	3	32,0	94,44				

Table 2 shows that cobalt is removed from iron quantitatively by means of cupferron, and is determined reasonably accurately.

SUMMARY

A technique has been developed for separating iron from small amounts of cobalt by extracting the former as its cupferronate with chloroform. The method has been checked by determining cobalt in soils; good results were obtained.

THE PHOTOMETRIC DETERMINATION OF ACETIC ACID IN THE PRESENCE OF OTHER ACIDS

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Of the numerous methods of determining acetic acid [1] the photometric method is the most selective. The method is based on the capacity of basic lanthanum acetate to give a color with iodine. Kruger and Tschirch [2] suggested this reaction for the qualitative detection of acetate ions; Cl^-, PO_4^{3-}, SO_4^{2-}, Ca^{2+}, Mg^{2+} and organic materials which reduced iodine interfere. It was subsequently found that lactic and pyruvic acids also interfere. Propionic acid, like acetic acid, gives a blue color. Under certain conditions the reaction mentioned can be used for the quantitative determination of acetic acid [3,4]. Hutchens and Kass [4] have determined microamounts of acetic acid in the media used for the culture of microorganisms. After removal of interfering inorganic materials, acetic acid can be determined with an accuracy of 3-5%. Fluoroacetic acid and other halogen-substituted acetic acids can be determined with the same accuracy.

In the work described here we used the method indicated for the rapid quantitative determination of acetic acid without removing it beforehand from the mixture of acids. We were interested in the possibility of determining acetic acid quantitatively in the products from the ozonolysis of vinyl acetylene hydrocarbons, i.e., in the presence of formic, trimethylacetic, and trimethylpyruvic acids, the concentrations of which corresponded to their content in the ozonolysis products.

As we established, trimethylpyruvic acid, like pyruvic acid, interferes with the determination by reducing iodine. Nevertheless, after oxidizing the trimethylpyruvic acid and distilling off the acetic acid by the method suggested below, the acetic acid can be determined with an error of 1-3%.

EXPERIMENTAL

Preparation of Solutions. 0.02 N aqueous iodine solution (2.54 g of chemically pure iodine and 33.2 g of chemically pure potassium iodide are dissolved in one liter of distilled water); 2.5% lanthanum nitrate solution [12.5 g of chemically pure $La(NO_3)_3$ in 500 ml distilled water].

Formic acid: commercial product.

Trimethylacetic acid (m.p. 34°) was synthesized from tertiary butyl chloride and carbon dioxide by Grignard's method.

Trimethylpyruvic acid (m.p. 90-91°) was prepared by oxidation of pinacoline with permanganate [5].

We used a calibration curve which was constructed using a solution of sodium acetate obtained by titrating an accurately weighed amount of acetic acid with 0.1 N NaOH.

All optical density measurements were carried out on a FÉK-N-54 apparatus using a No. 8 filter (transmission maximum at 656 mμ).

Experimental Procedure. One ml of solution containing 0.08-0.25 mg of acetate was introduced into a 5-6 ml test tube with a well-fitting ground stopper. One ml of 2.5% lanthanum nitrate was carefully added along the test tube walls, and this was followed by 0.1 ml of 0.02 N iodine solution and finally by 1 ml of 0.1 N ammonia solution. The contents of the test tube were heated for 5 min on a boiling water bath and were then cooled in a beaker of water and the optical density of the solution measured after 30 min in a cuvette with l = 1 cm. A control solution was prepared in parallel and the optical density of the colored solutions measured relative to it. It should be emphasized that the order in which the reagents are added must be strictly adhered to. Hutchens and Kass in their paper [4] re-

commend that a "combined" reagent be prepared by mixing equal volumes of ammonia and lathanum nitrate and adding 2 ml of the mixture obtained to the acetate solution. According to our observations, under these conditions the color only develops after standing for a long time or not at all. This can be explained by the fact that the basic lanthanum acetate originally formed and which is not capable of adsorbing iodine reacts very slowly with acetate. At very low acetate concentrations the color only develops after heating and has a slightly greenish tinge.

When trimethylpyruvic acid and acetic acid were present simultaneously, the acetic acid was determined after oxidation of the keto acid with chromic mixture. Twenty-five ml of solution containing a known amount of acetic and trimethylpyruvic acids, 0.5 g of potassium dichromate, and 1 ml of concentrated sulfuric acid were introduced into a 250-ml Kjeldahl flask fitted with a dropping funnel, a Kjeldahl adapter and a condenser. The mixture was heated for one hour to the boil. The acid products obtained were steam distilled and 0.1 N NaOH added until the pH was

Determination of Acetic Acid in the Presence of Other Acids

Amount of acetic acid, mg		Error		Ratio of the concentration of formic (I), trimethylacetic (II), and trimethylpyruvic (III) acids to acetic acid concentration		
taken	found	mg	%	I	II	III
29,50	29,21	0,29	0,98	—	—	—
11,79	11,52	0,27	1,29	—	—	—
23,60	22,71	0,89	3,77	10	—	—
17,71	17,36	0,35	1,97	10	—	—
29,50	29,32	0,18	0,61	—	8	—
23,60	23,12	0,48	2,03	—	11	—
73,87	73,75	0,12	0,16	—	—	5
21,93	21,63	0,31	1,41	—	—	10
29,50	29,12	0,38	1,28	5	10	3
23,60	23,56	0,14	0,59	10	10	10

8.2-10 as measured by a pH meter. The volume of the neutralized distillate was made up to 250 ml and the acetic acid determined as described above.

It is clear from the table that formic and trimethylacetic acids do not interfere with the determination, even when their concentration is ten times that of acetic acid. The error of the method described for determination of acetic acid is 1-3%.

SUMMARY

It has been established that it is possible to determine acetic acid photometrically in mixtures containing large amounts of formic and trimethylacetic acids. Acetic acid can only be determined in the presence of trimethylpyruvic acid when the latter has been oxidized beforehand.

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QUANTITATIVE DETERMINATION OF MONOFUNCTIONAL ALCOHOLS BY MEANS OF ACRYLONITRILE

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We showed in a previous paper [1] that acrylonitrile is a suitable reagent for the quantitative determination of thioalcohols and thiophenols. The reaction between acrylonitrile, thioalcohols, and thiophenols proceeds quantitatively in the absence of a catalyst. Further work on studies of the possibility of using acrylonitrile in organic analysis has shown that this reagent can be used for the quantitative determination of alcohols when the reation is carried out in an alkaline medium. Acrylonitrile reacts with alcohols according to the equation $ROH + CH_2 = CH \cdot CN \rightarrow ROCH_2CH_2CN$ [2].

By adding a known excess of acrylonitrile dissolved in dioxane to the reaction mixture and determining the excess of the reagent by the sulfite method we suggested earlier [3,4], it is possible to determine primary and secondary alcohols, and alcohols with certain other functional groups, quantitatively. In the cases of polyfunctional alcohols (ethylene glycol) only one of the hydroxyl groups reacts quantitatively in the cold. For primary alcohols the reaction is complete after 1hr to 1hr 30 min at room temperature, and 15-30 min at 35-40°; the reaction takes 3-6 hr at room temperature and 1 hour to 30 min at 35-40° in the case of secondary alcohols. An essential prerequisite is that the dioxane and acrylonitrile be carefully purified from peroxides and other impurities. Water interferes with the determination since it reacts with acrylonitrile in the presence of alkali.

The acrylonitrile is shaken with a sodium hydroxide solution; it is then dried first with potash, then with magnesium sulfate, and finally distilled. Dioxane is boiled under reflux for several hours with finely cut sodium metal and then distilled over sodium.

Results of determinations of alcohols are given in the table.

Experimental Procedure. About 1 mM of test alcohol is introduced into a 25-ml standard flask; 5 ml of dioxane is added, followed by 0.02-0.03 g of finely group potassium hydroxide. The flask is stoppered and carefully shaken until the alkali has dissolved completely, after which dioxane is added to the mark. One ml of the solution prepared is introduced into a ground-neck conical flask; 2 ml of 1 N acrylonitrile solution is added (72 g acrylonitrile in one liter of dioxane); the flask is stoppered and allowed to stand (for primary alcohols, 1 hour to 1 hr 30 min at room temperature or for 15-30 min at 35-40°; for secondary alcohols, 3-6 hr at room temperature, or for 1 hr to 1 hr 30 min at 35-40°).

After the reaction is complete, excess acrylonitrile is determined: 25 ml of 1 M sodium sulfite (240 g of the septihydrate in one liter of boiled distilled water) is added to the flask; this is followed by 5-7 drops of mixed thymolphthalein-alizarin yellow indicator (the indicator is prepared by mixing 30 ml of a 0.1% alcoholic solution of thymolphthalein with 15 ml of 0.1% aqueous alizarin yellow solution) and the liberated alkali titrated with 0.1 N hydrochloric acid until the blue color disappears and a yellow color appears.

A blank test is carried out simultaneously. Two ml of acrylonitrile is added to 25 ml of sulfite solution, and after 5 min, 1 ml of the prepared solution or test alcohol added. The solution is finally titrated with 0.1 N acid, using the same indicator.

Results are calculated by means of the formula

$$\% \text{ OH} = \frac{(a - b)\ N \cdot 17}{c \cdot 10},$$

where a and b are the number of ml of acid used for titrating the blank and the test solution respectively; c is the weight of alcohol taken; and N is the normality of the acid.

Test material	Time	Temperature, °C	% OH	
			Found	Calculated
Methanol	45 min	Room	53.10	53.06
	1 hr	"	52.98	
	20 min	30-35	53.10	
	20 min	30-35	53.04	
Ethanol	1 hr 45 min	Room	36.88	36.90
	1 hr 45 min	"	36.99	
n-Propanol	1 hr	"	28.25	28.29
	1 hr 45 min	"	28.32	
n-Butanol	1 hr 30 min	"	22.92	22.94
	1 hr 30 min	"	22.95	
	15 min	45	22.92	
	20 min	45	22.95	
n-Amyl alcohol	40 min	Room	19.28	19.28
	40 min	"	19.20	
n-Heptyl alcohol	1 hr 20 min	"	14.62	14.63
	1 hr 20 min	"	14.57	
	35 min	35-40	14.62	
	35 min	35-40	14.67	
Allyl alcohol	1 hr	Room	29.32	29.27
	1 hr	"	29.19	
Benzyl alcohol	15 min	"	15.71	15.73
	25 min	"	15.76	
Isobutanol	40 min	"	22.98	22.97
	40 min	"	22.88	
Isoamyl alcohol	40 min	"	19.29	19.28
			19.35	
Cyclohexylcarbinol	30 min	"	14.91	14.89
	30 min	"	14.88	
Phenyl ethyl alcohol	30 min	"	13.93	13.91
	30 min	"	13.85	
Phenyl propyl alcohol	30 min	"	12.54	12.48
			12.48	
Isopropanol	45 min	"	28.32	28.29
	5 hr 30 min	"	28.32	
Cyclohexanol	2 hr 30 min	"	17.02	16.97
	2 hr 30 min	"	16.98	
	1 hr	35-40	16.93	
	1 hr	35-40	16.93	
Secondary butanol	1 hr	35-40	22.97	22.97
	1 hr	35-40	22.83	
Hexanol-4	1 hr 30 min	35-40	14.63	14.63
			14.60	
Ethylene cyanhydrin	3 hr	Room	23.91	23.92
			23.93	
Ethyl cellosolve $CH_2(OH)CH_2(OC_2H_5)$	30 min	"	18.85	18.87
	30 min	"	18.87	

SUMMARY

A titrimetric method has been developed for the determination of primary and secondary alcohols, using their reaction with acrylonitrile in the presence of alkali.

The reaction takes some tens of minutes (at 35-40°).

The reaction is carried out in dioxane solution. The excess acrylonitrile is determined by the sulfite method.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

ANALYSIS OF BINARY MIXTURES OF TETRACHLOROALKANES

K. I. Sakodynskii and N. N. Umnik

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Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 3,
pp. 375-376, May-June, 1961
Original article submitted July 27, 1960

Analysis of mixtures of tetrachloroalkanes (TCA) obtained by telomerization of carbon tetrachloride with ethylene is a difficult problem. Thus, despite appreciable differences in the boiling points, during analysis of mixtures of TCA by analytical distillation on a fractional distillation column, a high degree of accuracy is not obtained. Moreover, a comparatively large amount of sample is required when this technique is used. Gas liquid chromatography would appear to be the most promising method for analysis of mixtures of TCA.

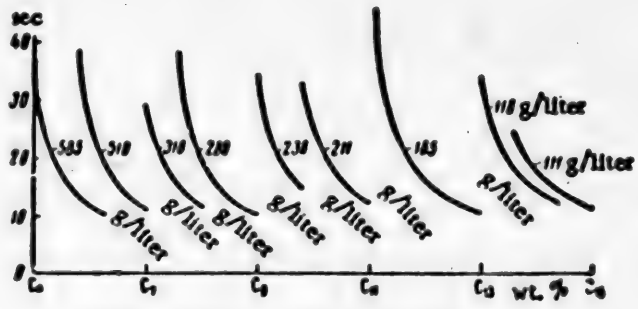
During studies of the distribution of adjacent TCA between different solvents during extraction, and determination of the partition coefficients of binary mixtures during evaporation, it is necessary to carry out a series of express analyses of binary mixtures of TCA. In such a case the simple and fairly accurate method of analysis developed in detail for the determination of the isotopic composition of water [1] is very convenient to use. The method is based on measuring the dropping time of drops of the test samples in a viscous medium. The dropping time is proportional to the density, which depends on the composition of binary mixtures of components with different densities. The density of the medium in which the drops are allowed to fall should be similar to that of the test samples in order that the dropping time is long enough for it to be measured. Since individual TCA have different densities, and the density difference amounts to 0.09 for C_5-C_7 mixtures and 0.02 for C_{15}-C_{17} mixtures, it is impossible to choose one medium which is suitable for the determination of the dropping time for all binary mixtures of TCA [2]. The most suitable media for measuring the dropping rate of drops of binary mixtures of TCA were found to be aqueous solutions of $Na_2S_2O_3$ for C_5-C_7 mixtures and NaCl solutions for C_7-C_{15} mixtures. Chemically pure reagents were used for preparing the requisite solutions, the NaCl concentration being subsequently determined argentimetrically and the $Na_2S_2O_3$ concentration iodometrically.

Calibration curves were constructed with the aid of standard mixtures of TCA, and the latter were prepared by weighing out aliquots of individual TCA; microburets were used for measuring out the aliquots so that the compositions of the mixtures differ from each other by approximately 10%. Pure, individual TCA obtained by a double distillation on a ladder-type laboratory column used for molecular distillation [13] were used for preparing the standard mixtures. In order to measure out drops of exactly the same size, a capillary of the type used for isotopic analysis of water was used. The test tube holding the solution had a diameter of 10 mm and was about 35 cm long. The test tube was immersed in a thermostat kept at 25 ± 0.1°. The thermostat temperature does not have to be controlled accurately because aqueous solutions are used. The dropping time was determined by measuring the time taken by a drop to pass two marks 15 cm apart. The dropping time was determined 10-12 times, results differing by more than ± 0.3 sec from the mean value as a result of random deviations in the size of the drops being rejected. Before measurement the mixtures were shaken, since it was found that on standing there was a tendency to fractionate according to density.

Since it was found that a medium with one density was insufficient for determination of the concentration of even one binary system with the requisite degree of accuracy, the concentration range measured was divided into two sub-ranges which overlapped. Solutions of the following concentrations were used: for C_5-C_7 mixtures, 585 and 510 g $Na_2S_2O_3$/ liter; for C_7-C_9, 318 and 280 g NaCl/ liter; for C_9-C_{11}, 238 and 211 g NaCl/ liter; for C_{13}-C_{15}, 118 and 111 g NaCl/ liter; and for C_{11}-C_{13}, 165 g NaCl/ liter. The calibration curves for the binary mixtures are shown in the figure.

When the calibration curves have been constructed, analysis reduces to determination of the mean dropping time. A check carried out on control samples showed that the method ensures an accuracy of ± 0.5-1% absolute, the accuracy being higher the greater the dropping time.

The method developed for the analysis of the composition of binary mixtures of TCA is rapid and gives results which are accurate enough. By introducing some improvements (using a longer measuring tube, and subdividing the concentration range into a larger number of subdivisions) it should be possible to enhance the accuracy of the method, should this be necessary.



Calibration curves for binary mixtures of TCA.

SUMMARY

A method for the analysis of binary mixtures of tetrachloroalkanes has been developed which is based on measuring the dropping time of test mixtures in a viscous medium. Dropping time is a function of density which depends on the composition of a binary mixture.

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CRITICISM AND BIBLIOGRAPHY

A. P. Alimarin and M. N. Petrikova, "Inorganic Ultramicroanalysis" Izd. AN SSSR, Moscow, 1960. 152 pp., 8,000 copies, price 6 rubles.

Reviewed by A. K. Babko

Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 3, pp. 377-378, May-June, 1961

Ultramicroanalysis (UMA) originated with biochemistry and later proved of considerable help in the development of radiochemistry. Undoubtedly the technique of this method could be useful for analytical chemistry, mainly in those cases where only a very small amount of test material is available, and also for examining analytical concentrates of microimpurities. Accordingly, the appearance of a short textbook on inorganic UMA in which a description is given of the basic techniques and possibilities of the method is very timely.

At the very beginning the authors emphasize that their aim is to describe the techniques and apparatus of UMA using known chemical and physicochemical methods. In UMA, concentration sensitivity remains almost the same as in macromethods; the absolute amount of test material can be reduced a thousand, tens of thousands, and hundreds of thousands times.

For working on the microscale, special apparatus and vessels are required, which the research worker often has to make himself. Of special importance is the large increase in relative surface. The basic apparatus – microscope, micromanipulators, piston attachments for micropipets, humidity cabinets, and some other apparatuses – are described very briefly, in about ten pages.

A large part of the book is devoted to questions of qualitative UMA. A description is given of the general technique for observing the formation of colored compounds, and individual techniques are also considered. From the tables included, it is clear, e.g., that when the thiocyanate reaction for iron is carried out on the macro scale the limit of identification is 10^{-5} g, while using UMA it is possible to detect 10^{-9} g. It should be pointed out that the authors at this juncture depart from their undoubtedly correct assertion that the concentration sensitivity depends on the physicochemical properties of the material formed, and not on the scale of the experiment. It follows from Table 6 that though the concentration sensitivity for the detection of iron by UMA increases ten times, the sensitivity of the detection of chromium increases by more than ten times. It must be assumed that in this case the authors are using insufficiently critically checked results, and one has to believe what the authors have written in the text.

The technique of observing certain precipitation reactions is described. The main techniques are described briefly but usually clearly enough. Some instructions are however incomprehensible. For example, it is difficult to imagine what is meant by the following: "... the cone plus precipitate are placed in a capillary fused at both ends and containing a drop of water."

In addition to the usual techniques of forming colored compounds, and of precipitation reactions, more than half the book is devoted to less well known UMA techniques such as deposition of metals by electrolysis, chromatographic methods, extraction with organic solvents from volumes of 10^{-3} - 10^{-5} ml, etc. Qualitative UMA of certain materials is described; the use of Russian-made apparatus for taking micro samples is interesting.

Only about one third of the book is devoted to quantitative UMA. In this section, in addition to the usual methods of gravimetric and titrimetric analysis, the use of electrochemical methods of titration, as well as of colorimetry and spectrophotometry, is discussed. It seems, despite what the authors say, that the impression is created that titrimetric UMA is a very difficult method. Naturally, the change-over from the usual scale of qualitative or gravimetric analysis to the UMA scale also requires some skill on the part of the analyst. Nevertheless, the experimental technique often reduces to carrying out simple operations by micromanipulators. The use of potentiometric and amperometric methods of titration in UMA would appear to be rather pointless. Thus, if any particular material can be titrated amperometrically this means that it could also be determined polarographically. Essentially, amperometric titration was developed with the aim of decreasing the sensitivity of polarography (the accuracy being increased

at the same time). If, then, one is seeking for ways of determining ultrasmall amounts, the use of amperometric titration cannot be regarded as the right approach; polarographic determination of microvolumes is considerably simpler than amperometric titration.

A more favorable impression is gained on reading the last section of the book, which is devoted to descriptions of colorimetric and spectrophotometric UMA methods. Here one has only to replace the usual cuvette by a microcuvette, the usual colorimeter or spectrophotometer by some other measuring apparatus, and this is easily done in practice.

From all that has been said it is clear that the apparatus and technique of UMA are presented widely, and the reader can gain a clear impression of the present state of these questions.

Among the defects of the book, indicated above, are the unjustified brevity of some sections, and insufficiently critical evaluation of some methods. Some more examples can be given. The authors are quite correct in some instances where they say that a detailed description is superfluous. Nevertheless, even in a short book, if it has been decided that a description should be given then it should be given clearly. Thus, why (and how?) "split a thick-walled capillary in two ..."(p.122) in order to make a holder for the vessel. This is incomprehensible.

In conclusion the authors give a short but interesting paragraph on the possible development of inorganic UMA. One cannot but agree with the views advanced here. Nevertheless, there should be some discussion of some supplementary problems. At least two other possible lines of approach can be mentioned which would help the development and extension of the application of UMA.

a) The use of sparingly volatile organic solvents. Difficulties associated with the rapid evaporation of micro drops of aqueous solutions are dealt with several times in the book under review. The difficulties are even greater when nonaqueous solutions are used; extraction requires special conditions and becomes extremely awkward. In UMA, however, many of these difficulties could be overcome by using such solvents as glycerol, nitrobenzene, supercooled salol and other solvents. At the same time the study of chemical reactions in such solvents would supplement our over-all chemical understanding.

b) One of the most valuable applications of UMA, as pointed out in the book, would be its use for the determination of microimpurities. Obviously, in such cases, the work would have to start with macrosamples and an analytical concentrate of the microimpurities prepared. The concentrate should then be analyzed by UMA. Taking into account the characteristic features of UMA, the conclusion can be drawn that the most valuable technique for the preparation of analytical concentrates would probably be the method of organic coprecipitants suggested by V. I. Kuznetsov; were such a technique used after combustion, the ultramicro amount of test impurity thus obtained directly could then be analyzed by UMA. Such methods, however, have not as yet been developed.

On the whole, the book under review is of undoubted interest and enriches our literature on analytical chemistry.

A. Okac, "Qualitative analytische Chemie"
Akademische Verlagsgesellschaft, Leipzig, 1960. 644 pp.

Reviewed by I. N. Marov

Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 3, pp. 378-379, May-June, 1961

This book was first published in 1956 in Prague in Czech, and it was published in German by the Leipzig Academic Press in 1960. In this edition a number of chapters in the book have been expanded appreciably, and it includes a new chapter on physical methods in analytical chemistry. The appearance of a new edition of the book is to be welcomed since there has long been a need for a modern textbook on qualitative analysis.

The book contains some brief information on the history of analytical chemistry and the development of qualitative chemical analysis; the most important theoretical questions relating to qualitative analysis, the technique of carrying out qualitative and microcrystalloscopic reactions are discussed, etc. A number of new group and selective reactions are described in addition to the classical group reactions.

Sodium carbonate, acetate, and phosphate, potassium chromate, hydrochloric and sulfuric acids, etc., are used as group reagents as well as organic materials (hydroxyquinoline, anthranilic acid, dithizone, cupferron, etc.).

A considerable part of the book (300 pages out of 640) is devoted to selective reactions. This section is very rich in material on selective reactions for almost all elements. A number of such reactions are given for each element, and, as a rule, possibilities are indicated of direct establishement of the presence or absence of a particular element in test samples.

The last chapter, which is devoted to a review of some physical methods used in analytical chemistry, should in the author's opinion serve as a short textbook, by means of which a chemist should be able to choose the method he wants. One of the best features of the book is the vast bibliography (945 references) given at the end of the book. It covers the literature up to 1958.

Okač's book has taken into account modern achievements in theory and practice and is a valuable textbook on qualitative analysis for students in chemical faculties and for analytical specialists.

Houben-Weyl, "Methoden der organischen Chemie"

Reviewed by V. G. Tiptsova

Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 3, p. 379, May-June, 1961

Methoden der organischen Chemie (Houben-Weyl). Vierte völlig neu gestaltete Auflage. Herausgegeben von E. Müller. Unter besonderer Mitwirkung von O. Bayer, H. Meerwein, K. Ziegler. Verlag G. Thieme, Stuttgart.

Bd. 1/2. Allgemeine Laboratoriumspraxis. Teil 2. Bearbeitet von A. Berthmann, K. Blumrich, W. Büche, W. Bunge, R. Jaecker, H. Jonas, ... 1959, 1017 pp.

Bd. V/4. Halogenverbindungen. Brom- und Jodverbindungen – Herstellung. Chlor-, Brom- und Jodverbindungen –Reaktivität, Umwandlung. Bearbeitet von N. Kreutzkamp, H. Meerwein, A. Roedig, R. Stroh, 1960, 894 pp.

Bd XI/2. Stickstoffverbindungen II. und III. Bearbeitet von H. Bestian, L. Birkhofer, A. Dorlars, H. Freytag, ... 1958, 840 pp.

The second part of the first volume of Houben-Weyl's reference work is devoted to general laboratory methods. Among the various questions which are examined in detail are modern methods of preparing, purifying drying, and storing gases, while the technique of working with liquefied gases in an inert gas atmosphere and the technique of working with small amounts of material at low pressure are described. The properties and purification of the most important organic solvents are discussed, as well as drying techniques.

The fourth part of the fifth volume is devoted to a detailed review of methods of preparing bromine- and iodine-containing compounds, and to the various transformations of organic compounds of chlorine, bromine, and iodine. The second part of the eleventh volume is devoted to the various transformations of amines, 1,2- and 1,3-alkylene-amines, amino acids, and lactams. There is a wealth of information on quaternary ammonium bases and on compounds containing nitrogen and sulfur.

The volumes of Houben-Weyl under review, like those published earlier[see Zhurnal analit. khimii 13, 376 (1958)], contain a very large bibliography and the well-compiled index is set out extremely well.

The new edition of this fundamental reference work of Houben-Weyl with its wealth of valuable material is of great interest not only for analytical chemists working on synthesis and studying new organic reagents but also for organic analytical chemists. The material on general laboratory methods is valuable for a wide circle of chemical research workers.

OBITUARY

YURII VITAL'EVICH MORACHEVSKII

Soviet chemical science suffered a heavy loss on January 4, 1960. On that date Professor Yurii Vital'evich Morachevskii died; he was outstanding in the field of analytical chemistry, geochemistry, and halurgy, he was head of the chair of analytical chemistry at Leningrad State University and of the analytical laboratory of the Institute of Silicate Chemistry, Academy of Sciences, USSR. He was also a member of the Commission on Analytical Chemistry, Academy of Sciences, USSR and a doctor of chemical sciences.

The scientific research work of Morachevskii is distinguished by its exceptional breadth and variety, although it was concentrated on problems relating to an all-round study of mineral raw materials. His scientific activity was closely connected with the solution of important practical problems in the social economy. During his life Morachevskii combined his scientific research with a large amount of teaching and organizational activity.

Morachevskii was born on July 11, 1894. He finished at Leningrad university in 1917 and started to work at the All-Union Geological Institute (Geological Committee) as an analytical chemist, and later became a scientific group leader and head of the geochemical section. During the middle twenties, with the turbulent growth of geological prospecting work in the USSR, the chemical laboratory of the Geological Institute under the direction of Morachevskii also expanded– from a group consisting of a few analysts to a large scientific reasearch establishment including eight special laboratories and about 150 co-workers. At the same time, Morachevskii was responsible for organizing dozens of laboratory field parties, instructing analytical chemists, and personally conducting experimental work developing new methods of analyzing many types of mineral raw material. Yu. V. Morachevskii was one of the fundamental organizers of chemical service in geology.

Morachevskii initiated the publication and was the chief editor and author of many sections of the reference work "Analysis of Mineral Raw Material," in which the experience of many analytical chemists was collected. The second edition of this work, considerably revised and supplemented, was brought out in 1956 under the editorship of Morachevskii and Yu. N. Knipovich.

Morachevskii, as a geochemist, was widely known for his studies of salt deposits of the Soviet Union. His most important works, "Features of the Geochemistry of the Verkhnekamsk Salt Deposits," "Conditions for the Formation of Deposits in the Solikamsk Lagoon," "Gas-Bearing of Potassium Salts of the Verkhnekamsk Deposits," and a number of others, are parts of a single, broadly developed work dealing thoroughly and for the first time with the geochemistry of the Solikamsk Deposit of potassium salts, the largest in the world.

One must include the huge amount of work which Morachevskii carried out, and the help he gave in connection with exploring and planning the construction of the Solikamsk Hydro Projects and a number of other large hydrotechnical constructions.

In the course of his work in the Leningrad Mining Institute (1936-1941) Morachevskii carried out important research on the copper-nickel ores of the Trans-Polar region, their geochemistry, the distribution of accompanying elements in them, and their behavior during metallurgical processing.

With his wide knowledge and huge experience Morachevskii was closely connected with the many institutes in Leningrad and other cities.

For many years Morachevskii led a very fruitful teaching career. From 1944 he was head of the school of analytical chemists at Leningrad University and contributed immensely to the education of young scientists. Morachevskii reorganized the teaching of analytical chemistry in Leningrad University, organized a course on the theoretical bases of analytical chemistry and the analytical chemistry of the rare elements, and introduced a number of new specialist courses and practical work to the chair. Morachevskii tried to educate analysts with a broad outlook, possessing a knowledge of the basic methods of modern analytical chemistry.

The main subject at the chair of analytical chemistry was the analytical chemistry of mineral raw materials, particularly questions relating to the analytical chemistry of rare and scattered elements. This naturally encompased a wide range of analytical methods, and Morachevskii saw that it would provide rich training for young analytical chemists. He gave a lot of attention, particularly during the last years of his life, to methods of teaching analytical chemistry, to a correct definition of the problems of analytical chemistry as a science, and to the possibilities of its further development.

In 1950 Morachevskii organized the analytical laboratory in the Institute of Silicate Chemistry, Academy of Sciences, USSR. During the first years of the existence of the laboratory the work carried out was devoted to individual problems relating to the determination of the main components of silicates. In later years, under the direction of Morachevskii, the laboratory moved on to a research plan which he had worked out for developing and improving methods for determining microamounts of various elements in silicates and in elemental silicon.

Spectrochemical methods of determining a number of microimpurities in specially purified material – silica and semiconducting silicon – which were developed under the direction of Morachevskii are distinguished by their high sensitivity. Recently, work has started under Morachevskii's direction on the radioactivation determination of impurities in specially purified silica. To solve these problems, on the initiative of Morachevskii, a well equipped laboratory of spectrochemical analysis and radioactive isotopes has been set up in the Institute of Silicate Chemistry.

As a member and vice-chairman Morachevskii has contributed largely to the organization and work of the D. I. Mendeleev All-Union Chemical Society, particularly in his own Leningrad Branch. He has lectured often on current problems in chemical science and on the philosophy of natural science.

Despite the poor state of his health, not sparing his strength, he enthusiastically and with deep consciousness of service carried out his numerous duties, right up to the last moment.

The shining image of Yurii Vitalevich, an outstanding scientist, a talented leader and educator of youth, and a charming personality will always stay in the hearts of his numerous pupils and friends.

The Commission on Analytical Chemistry, Academy of Sciences, USSR
Institute of Silicate Chemistry, Academy of Sciences, USSR
A. A. Zhdanov Leningrad State University
Leningrad Branch of the Mendeleev Chemical Society
Editorial Board of "Zhurnal analiticheskoi khimii"

Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 3, pp. 380-381, May-June, 1961

EVENTS

PROBLEMS OF MATERIAL (CHEMICAL PHASE) ANALYSIS AT THE CONFERENCE ON METHODS OF ANALYZING SELENIUM-CONTAINING ELEMENTS

B. S. Khristoforov

Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 3, pp. 382-383, May-June, 1961

The possibility of establishing the form in which rare and scattered elements occur has hitherto been open to doubt because the chemical properties of these elements have not been studied in sufficient detail, and because of the low concentrations at which they occur. Despite this there has been an increasing number of references published recently on this type of investigation. Nevertheless, the information published on such work is often not complete enough, so that the results of such work cannot be used for developing technological schemes of extracting selenium even during the control of the appropriate processes. In this connection, it is not unimportant that on the initiative of N. S. Greiver and B. V. Dolivo-Dobrovol'skii at a conference held on June 22-27, 1960 at the Leningrad Mining Institute with the purpose of exchanging experience on the application of various methods of determining selenium, tellurium, and the elements which accompany them, a special group of reports and communications was given which dealt with methods of determining the form in which selenium exists in different production materials.

In all, five reports and communications were read at the conference on these questions.

Co-workers at the Central Laboratory of the Leninogorsk Polymetallic Combine V. V. Malakhov, E. D. Glotko, E. I. Savichev, et al., gave a report on the subject "Determination of the Form of Selenium Compounds in Dusts and Distillates from Lead Production."

As the result of studying the elemental composition of dusts from lead production and some products from their processing, as well as the physicochemical conditions for the formation of these products and the values of the heat of formation of different forms of selenium, the authors have suggested that selenium may be present in the dusts and distillates in its elemental form, in the form of its dioxide, and also in the form of the selenates, selenites, and selenides of lead, zinc, mercury, and some other metals. In order to check this assumption, the authors synthesized the compounds listed and studied some of their chemical properties, in particular the action of water on them, and also the action of alkalis, mineral acids, sodium sulfide and sulfite, hydrogen peroxide, and some other reagents.

Comparison of the results obtained enabled the authors to suggest, after a careful check on various production materials, a method for determining the form in which selenium occurs in dusts and distillates from lead production and in certain products obtained during the processing of these materials.

B. S. Khristoforov and R. M. Monasypova (Altai Mining-Metallurgical Scientific Research Institute, Academy of Sciences, Kazakh SSR) in a communication on "The Forms of Selenium in the Sludge from Sulfuric Acid Production at the Ust'-Kamenogorsk Lead-Zinc Combine" showed that it was possible to apply the technique for determining the form in which selenium occurs developed at the Central Laboratory of the Leninogorsk Polymetallic Combine to the study of sulfuric acid sludge from the plant operating on roasting gases from zinc production. It was established that the greater part (up to 70%) of the selenium is present in the sulfuric acid sludges UK STSK in the form of a complex sulfido-selenide of mercury and tin of the type (Hg, Zn) (S, Se) and about 25% in the form of simple lead and zinc selenides.

N. A. Filippova reported on a technique developed at Gintsvetmet for establishing the form in which selenium is present in dusts from lead production.

V. V. Dolivo-Dobrovol'skii and T. N. Greiver (Leningrad Mining Institute) gave a long report on "The Possible Forms of Selenium and Tellurium in Copper Electrolyte Platinum-Containing Sludges"; this report included a detailed description of methods for preparing selenium-containing compounds of silver, palladium, and copper, and also methods and experimental results of a study of the chemical properties of the selenides and selenites of the metals

listed. On the basis of the results obtained the authors have developed a technique for determining the content of the enumerated forms in which selenium occurs in the sludges.

Ya. L. Satin and A. P. Meliksetyan (Scientific Research Mining-Metallurgical Institute, Sovnarkhoz Armenian SSR) read a report on "The Determination of Selenium and Tellurium Compounds in the Products from the Sulfating Roasting of Copper Electrolyte Gold-Containing Sludges." They suggested a rational method of analysis which permits determination of selenium dioxide, elemental selenium, tellurium dioxide, silver and copper sulfates, and also the selenides of these metals on one sample.

The participants at the conference listened with interest to reports on development of methods of chemical phase analysis for selenium and tellurium compounds in products from the metallurgical processing of copper-nickel, copper, lead-zinc, and sulfuric acid products. The conference noted the first successes achieved in this field. The hope was expressed that there would be further developments in scientific research work along these directions.